Self-assembly has emerged as the strategy of choice toward generating ordered arrays of nanosized particles. The resulting materials—in particular, those assembled from inorganic nanoparticles (NPs) (1–7)—often exhibit unanticipated optical (8), thermoelectric (9), magnetic (10), catalytic (11), and other (12) properties. The diversity of structures and presumably the properties of these materials could be greatly enhanced via postsynthetic modifications, which could be used to generate assemblies in which the constituent NPs are ordered yet separated by relatively large distances—that is, non–close-packed (NCP) NP arrays. Although several examples of related materials have been reported, they are limited to highly specific systems, such as those involving highly directional interactions (13, 14) or a fine balance between attractive and repulsive forces during self-assembly (15). Thus, a general route to NCP NP arrays has been lacking.

One strategy to tackle this limitation could be based on the selective removal (by means of chemical etching) of one type of NPs from binary NP superlattices (BNSLs) (1). Depending on the stoichiometry and structure of the initial BNSLs, this method could lead to “nanoallotropes”—materials that have the same chemical composition but differ in their nanoscale architecture. Unfortunately, within BNSLs the two types of nanoscopic components mutually support each other, and removal of one would inevitably lead to the disruption of the other. Here, we hypothesized that this undesired behavior could be overcome by stabilizing the BNSL through controlled removal of the surfactants from the NP surfaces (16–18). If successful, this procedure would serve three purposes: (i) attaching the NPs to the underlying surface, (ii) controlling the coalescence of the NPs, and (iii) activating the sacrificial component of the BNSL toward etching.

We worked with monodisperse batches of Au and Fe$_3$O$_4$ NPs (figs. S1 and S2) (19), which we assembled at the diethylene glycol (DEG)—air interface (Fig. 1A, step 1), as previously reported (20). After transfer onto a carbon-coated transmission electron microscopy (TEM) copper grid (Fig. 1A, step 2) and a controlled, thermally induced desorption of ligands from the NPs (Fig. 1A, step 3) (17), the samples were exposed to an etchant solution to etch the remaining Au NPs (Figs. 1A and fig. S10) (17). To decipher the structure of this other more complex assemblies, we conducted electron tomography studies (23, 24) by acquiring series of two-dimensional (2D) projections of the etched arrays over a wide range of tilt angles using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). These studies confirmed that each cluster was composed of five Au NPs (giving rise to stoichiometry vacAu$_4$) (figs. S13 to S15) (19), and they helped elucidate the mutual packing of the resulting tetrahedra (Fig. 2, C and D, and database S1, tomography data) (19). The high stability of these tetrahedra could be attributed to partial coalescence of Au NPs, which occurred as a result of ligand desorption (16–18). As shown in the structural model in fig. S16, the vacAu$_4$ array is derived from an incomplete (deficient in Au) AB$_5$-type BNSL (19).

Our method allowed us to control the degree of coalescence by adjusting the time of thermal treatment: extending the heating time from 30 min to 6 hours allowed us to convert an ensemble of tetrahedra into a well-defined array of pseudospherical ~9-nm gold NPs (figs. S17 to S19) (19). An unexpected effect of heating was that Au NP quintets that lack a strong attachment to the underlying substrate could migrate and be transformed into well-defined sinus nanowires (fig. S20) (19).

Increasing the Au:Fe$_3$O$_4$ NP ratio to ~10 led to another type of BNSL, which, after the removal...
of Fe₃O₄, exhibited features (Fig. 2, E and F, and figs. S21 to S23) reminiscent of the previously reported (25) AB₁₃-type BNSL. The AB₁₃-type BNSL is composed of layers of quartets and quintets of the “B” NPs, following a (-B₄-B₇-B₄)ₙ pattern. However, electron tomography studies on our etched material revealed that it consisted of alternating layers of NP quartets and septets (a (-B₅-B₇-B₅)ₙ pattern) (Fig. 2, G and H), corresponding to an AB₇ stoichiometry of the precursor BNSL (fig. S24, discussion) (19). Similar to the AB₇-type BNSLs, the AB₅ arrays could be thermally transformed by partial sintering of the constituent Au NPs, resulting in nanoporous membranes (fig. S25, bottom) (19).

When the ratio of Au to Fe₃O₄ NPs was decreased to ~4 and a more polydisperse batch of Au NPs (~4.9 ± 0.7 nm) was used, we observed the formation of BNSLS, within which the Au NPs were arranged into zigzag-like patterns (fig. S26) (19). Electron tomography analysis showed that this BNSL consisted of stacked NP layers having an AB₄ stoichiometry (Fig. 2l and figs. S27 to S29) (19), where “A” denotes a Fe₃O₄ NP and “B” denotes large, medium, and small Au NPs in a 1:2:1 ratio (for example, the NCP array shown in Fig. 2l consists of 6.2-, 5.3-, and 4.1-nm Au NPs). The fact that highly crystalline arrays could be assembled even from relatively polydisperse batches of NPs highlights the tendency of NPs to maximize the packing at the DEG-air interface. Analysis of the AB₄, AB₆, and AB₁₁ BNSLs showed that they all share the same densely packed initial (bottom) monolayer [Fig. 2, D, H, and I, and figs. S16, S25, and S29, structural models (19)].

The formation of the above AB₄, AB₆, AB₁₁, and other structures not observed during self-assembly in three dimensions (bulk solution) suggests a profound effect of DEG on the assembly process (26, 27). To disclose the mechanisms that govern self-assembly in our system, we performed precise atomistic molecular dynamics (MD) simulations of NPs at different liquid-air interfaces. These simulations, detailed in the supplementary Materials, revealed that the role of DEG in guiding NP self-assembly is the result of a combination of several effects (19). First, the coupling energies of both types of NPs to DEG are large compared with the NP-NP coupling energies between exposed or partly submerged NPs (tables S1 and S2) (19). Hence, the NPs exhibit a high affinity to the surface of the underlying liquid, which they tend to cover in the most efficient way. Analysis of BNSLS assembled on the surface of DEG showed that as much as >50% of the lattice energies originates from NP-DEG, rather than NP-NP coupling (19). Second, both dodecanethiol-protected Au NPs and oleate-protected Fe₃O₄ NPs preferentially submerge in DEG to about half their diameter (Fig. 2, J to L). As a result, DEG can organize the bottom layer of NPs in a way that may not be achievable during self-assembly in bulk solution. Last, the coupling energy of the NPs to DEG per unit surface area of NP is approximately the same for both types of NPs. Thus, both Au and Fe₃O₄ NPs have a similar affinity toward the surface of DEG, from which they can displace each other during the self-assembly process. Taken together, these effects show that DEG can modify the free energies of BNSLS, favoring the formation of otherwise unstable BNSLS.

When the same polydisperse (~4.9 ± 0.7 nm) Au and monodisperse 10.6 nm Fe₃O₄ NPs were used in a ~5:1 ratio, we observed the formation of an unprecedented quasi-ternary BNSL with a stoichiometry ABC₅, where “B” denotes a small (~4.0 nm) and “C” denotes a large (~5.5 nm) Au NP (fig. S30) (19). Subjecting this superlattice to our stabilization-etching procedure afforded a NCP vacAu₄Au′ array shown in Fig. 2, M to P (here, Au and Au′ denote small and large Au NPs, respectively) (figs. S31 to S34) (19). Within the ABC₅-type BNSL, the bottom-most Au and Fe₃O₄ NPs have their bottom boundaries (rather than the equatorial cross sections) at the same level. However, the “half-submergence condition” is still satisfied for both NP types if one considers the two 5.5-nm Au NPs placed on top of each other (in Fig. 2P, C and C′) as a single, elongated NP. Electron tomography studies could not resolve individual NPs within these putative dimers, suggesting that they undergo a partial coalescence (Fig. 2O, blue and red).

Our methodology could be extended to multilayers (figs. S35 to S44) (19), which is exemplified for a novel AB₄-type BNSL (Fig. 3A and figs. S40 and S44) (19). This BNSL was obtained
by co-assembly of 5.2 nm Au and 10.6 nm Fe₃O₄ NPs premixed in a ~4:1 ratio, in which the thickness of the superlattice depended on the amount of NPs applied at the liquid-air interface. For example, HAADF-STEM tomography revealed that the NCP superlattice shown in Fig. 3B obtained by etching the corresponding BNSL (Fig. 3A) was a hexalayer (Fig. 3C, fig. S43, and database S1) (19). Upon extended (>1 hour) heating at 70°C, the original AB₄-type array was transformed into the exotic pattern shown in Fig. 3D (fig. S42) (19), whose structure remains
to be identified. Detailed theoretical analysis in the supplementary materials confirms that our technique can in principle be extended to NCP arrays having thicknesses approaching macroscopic dimensions (19).

Our methodology can also be applied to NP building blocks of other sizes. For example, in Fig. 3, F and G, we extended the average distance between 5.2-nm Au NPs within vac1Au1 arrays from 12.5 to 15.3 nm by simply increasing the size of the Fe3O4 NPs with which they were co-assembled from 10.6 to 13.0 nm. These results indicate the ability to pattern solid substrates with nanoscopic Au domains, with subnanometer precision. When the sizes of both Au (5.2 nm) and Fe3O4 (10.6 nm) NPs were decreased (to 3.0 and 8.4 nm, respectively), many of the BNSLs and the resulting NCP arrays could be recreated on a smaller scale (fig. S45) (19). Similarly, working with mixtures of 5.2-nm Au NPs and 8.4-nm Fe3O4, we obtained AB-, AB4-, and ABC4-type and other BNSLs described above (fig. S46) (19). In addition, the modified NP size ratio resulted in novel NP arrays, such as the vac1Au4-type and the vac2Au1-type structures shown in Fig. 3, H and I (fig. S47) (19). The main drawbacks of our method lie in the inherent difficulties in preparing defect-free BNSLs, which limited the size of single-crystalline domains of BNSLs, and hence of NCP arrays, up to several micrometers. In addition, it has proven challenging to control the film thickness throughout the entire area of the sample—for example, a 1:1 mixture of Au and Fe3O4 NPs predicted to give rise to a monolayer of the AB-type BNSL afforded a ~20:1:1 mixture of monolayer, bilayer, and noncoated substrate.

We envision that NCP NP arrays will have a wide range of interesting optical, mechanical, catalytic, and other properties. As an example, we examined several different NP arrays as substrates for surface-enhanced Raman scattering (SERS) and found that the vac1Au4T-type array has superior signal enhancement properties, as compared with that of vac1Au4 (Fig. 4). This is in agreement with a significantly higher density of electromagnetic hot-spots at nanometer-sized gaps between NPs within the multilayer structure, into which analyte molecules can readily diffuse through the NCP crystalline lattice (19). An attractive avenue will be to use the well-defined nanopores within these materials for trapping active protein molecules. Our procedure leads to surfactant-free Au surfaces, amenable to facile functionalization with thiolated ligands. Our results on multilayers suggest that this method could be readily extended to 3D assemblies, including binary superlattices comprising nonspherical NPs (28), quasicrystalline arrays (29), and ternary superlattices (30).
REFERENCES AND NOTES

19. Materials and methods are available as supplementary materials.

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SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/358/6362/514/suppl/DC1
Materials and Methods
Supplementary Text
Figs. S1 to S52
Tables S1 to S5
Caption for Database S1
References (31–52)
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Tunable porous nanoallotropes prepared by post-assembly etching of binary nanoparticle superlattices
Thumu Udayabhaskararao, Thomas Altantzis, Lothar Houben, Marc Coronado-Puchau, Judith Langer, Ronit Popovitz-Biro, Luis M. Liz-Marzán, Leila Vukovic, Petr Král, Sara Bals and Rafał Klajn

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Non–close-packed nanoparticle arrays
Films of colloidal nanoparticles usually form dense, close-packed lattices. If binary lattices could be made and one component removed, then a more open array could form, as long as the remaining nanoparticles could be stabilized. Udayabhaskararao et al. formed binary superlattices of gold and magnetite nanoparticles at an air-liquid interface that could then be transferred to carbon-coated surfaces (see the Perspective by Kotov). Selective etching of either of the nanoparticles created non–close-packed arrays with vacancies stabilized by the carbon surface.

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