The assembly of plasmonic nanoparticles into ordered 2D- and 3D-superlattices could pave the way towards new tailored materials for plasmonic sensing, photocatalysis and manipulation of light on the nanoscale. The properties of such materials strongly depend on their geometry, and accordingly straightforward protocols to obtain precise plasmonic superlattices are highly desirable. Here, we synthesize large areas of crystalline mono-, bi- and multilayers of gold nanoparticles >20 nm with a small number of defects. The superlattices can be described as hexagonal crystals with standard deviations of the lattice parameter below 1%. The periodic arrangement within the superlattices leads to new well-defined collective plasmon-polariton modes. The general level of achieved superlattice quality will be of benefit for a broad range of applications, ranging from fundamental studies of light–matter interaction to optical metamaterials and substrates for surface-enhanced spectroscopies.
Ordered arrays and superlattices of nanoparticles (NPs) have a huge potential for new materials with tuneable electrical, optical, and mechanical properties\(^\text{1-13}\). Common strategies to produce such structures include lithography-based nanofabrication\(^\text{14-16}\), and self-assembly of NPs functionalized with polymers\(^\text{10}\), DNA\(^\text{17-22}\), or dendritic molecules\(^\text{23,24}\). The ability to control both, the structure of the NP building blocks and the geometry of the superstructure might lead to designer materials with, for example, topological states and Dirac micrribands in the case of semiconductor NPs\(^\text{25,26}\). However, the transition from localized to the required delocalized electrons is often hindered by the lack of periodic order, size variations and, most importantly, the insufficient degree of electronic coupling between the NPs\(^\text{27}\). This can in part be circumvented by coupling the electromagnetic (dipole) fields instead of electrons. Then, scale and order of the superlattice can lead to new collective properties\(^\text{28-30}\). For example, the superfluorescence from periodically coupled excitonic dipoles of perovskite NPs was recently demonstrated\(^\text{31}\). In similar ways, plasmonic dipoles of metal NPs interact via dipole-dipole interactions\(^\text{30,32-34}\). This creates a continuum of collective plasmonic states where the electrons of the metal NP crystal remain localized. According to recent experiments, the coupling strength of such periodically coupled plasmons to photons can become comparable to the photon energy\(^\text{35}\). The optical properties are expected to be widely tuneable through crystal symmetry and geometry\(^\text{35-37}\).

A prerequisite for the formation of well-defined coupled modes is the uniformity of the constituents and a high degree of order on relevant scales (optical wavelength). The coupling strength increases with decreasing interparticle spacings, gaps <10 nm are favorable\(^\text{33,38}\). Upon today, it has been difficult to combine a high particle uniformity (size and shape) with a high degree of periodic order and large crystalline areas in the desired geometry. For small NPs (diameters <15 nm), a huge variety of mesoscopic superlattices have been reported\(^\text{5,10-12,39-51}\). However, most reports of these NP superlattices focus on the structural and electronic properties. The few optical studies exploiting the periodic order of plasmonic components, e.g. use lithographic structures as waveguides, where plasmons couple over much longer distances\(^\text{34,52}\). The reason for the lack of reports on periodic plasmon coupling is that there exists no robust protocol to assemble large plasmonic NPs like gold NPs (AuNPs) into large-scale crystalline superlattices. The plasmonic dipole strength, which is relevant for the periodic coupling, scales with particle size, yielding small AuNPs less attractive for periodic dipole field coupling. For example, to observe well-defined plasmon polaritons, the minimum AuNP diameter is ~25 nm\(^\text{36,53,54}\).

In this work, we present a robust protocol for assembling large (diameter > 20 nm) AuNPs into crystalline superlattices up to >0.01 mm\(^2\) for monolayers and even larger crystalline bilayer and multilayer with interparticle gaps in the range of 1–8 nm and standard deviations of the lattice constant of below 1%. This degree of order allows well-defined collective plasmon-polariton modes to emerge: we compare the film properties with the ones of less ordered, conventional films of comparable scales and demonstrate how order leads to the formation of new polariton excitations.

**Results**

**AuNP synthesis and functionalization.** Periodically coupled plasmonic modes require a continuous lattice of uniform NPs. NP size and shape deviations are disadvantageous for two reasons: they result in local variations of the (size-dependent) plasmonic properties and reduce the periodicity of the NP superlattice. To reproducibly obtain superlattices with interparticle gaps below 10 nm, our strategy therefore was to synthesize AuNPs with optimized dispersity and uniformity using the cetyltrimethylammonium chloride (CTAC)-based seeded growth strategy presented by Zheng et al.\(^\text{55}\). The AuNPs were functionalized with polystyrene-thiol ligands (PSSH) that have sufficiently low molecular weights (~2000, 5000, and 12 000 g mol\(^{-1}\); PSSH12k, PSSH5k, and PSSH112k) to allow for small interparticle gaps. At the same time, they still provide the stabilization that is necessary for high particle concentrations and stable assemblies in the desired diameter range. In a previous study we tested the potential of PSSH-promoted self-assembly with citrate-stabilized AuNPs (AuNP@Citrate) with dispersities (rSD) of ~8%. Despite some promising results, the limitations discussed above were encountered\(^\text{49}\). AuNP@CTAC have a more challenging surface chemistry and are obtained in lower yields than AuNP@Citrate but exhibit superior uniformity and lower dispersivity. The CTAC-based protocol was scaled up by a factor of 10 to obtain sufficient final concentrations. Phase-transfer-based ligand exchange as described for AuNP@Citrate does not work for AuNP@CTAC\(^\text{56}\). Therefore, AuNP@CTAC were functionalized with PSSH by a ligand exchange in THF, transferred to toluene, purified and concentrated for self-assembly experiments. The ligand exchange and the colloidal stability of the functionalized AuNPs were monitored by UV/Vis spectroscopy.

AuNP superlattice films were prepared by evaporation of AuNP solutions in toluene on a liquid subphase: diethylene glycol (DEG), as presented by Dong et al. for smaller NPs\(^\text{57}\). A scheme and resulting exemplary superlattice films are shown in Fig. 1. The straightforward protocol starts by pipetting of the AuNPs in toluene onto the DEG subphase in a Teflon or high density polyethylene (HDPE) well (Fig. 1a). The well is then covered with a cover slip and left undisturbed. Superlattice films usually form within 16–24 h (Fig. 1b) and can then be transferred onto arbitrary substrates like transmission electron microscopy (TEM) grids, glass slides, or silicon wafers. The superlattices can also form freestanding films (~40 μm × 40 μm, Supplementary Fig. 1).

All AuNP samples formed well-ordered AuNP superlattices, differing in the number of layers ranging from monolayer to multilayer (>20), number of defects, crystallite size and the crystal mosaicity (Fig. 1c-g and Supplementary Figs. 2–11). For all superlattice films, defect-free monolayers in the μm\(^2\) range were routinely observed (Fig. 1 and Supplementary Figs. 2–11) up to monolayers with long-range periodic order over areas >10,000 μm\(^2\). Even larger areas were obtained for crystalline bilayers (Fig. 1f and Supplementary Figs. 2–4, 6, 10, 11). Table 1 lists the studied samples with the concentrations c used for superlattice preparation and the interparticle edge-to-edge distances (gaps) in the formed superlattices determined by TEM and small-angle x-ray scattering (SAXS).

The gaps obtained by SAXS deviate up to a few nm from those obtained by TEM analysis. This observation points at the limits of the TEM analysis accuracy, especially for the larger AuNP which are slightly less uniform (cf. Supplementary Figs. 2–11)\(^\text{58}\). Consequently, complementary SAXS measurements for comparison are recommendable for the characterization of superlattices in general. AuNP superlattices covering large areas have been reported in several pioneering studies and recent reviews are available\(^\text{40,39-47,59,60}\). But the crystalline order presented herein is unprecedented to the best of our knowledge. With increasing number of layers, the superlattices can be described as well-defined AuNP-supercrystals (Fig. 1g and Supplementary Fig. 12).

The number of layers cannot be controlled perfectly, but as a tendency slow evaporation and an increasing number of particles in the drying solution seem to favor higher fractions of multilayer superlattices. Accordingly, a fast evaporation and low AuNP concentrations favor the formation of monolayers. Quantitative statements are not possible because the exact fractions of the
AuNP@PSSH

Cover slip Evaporation
of toluene

>16 h

DEG

Fig. 1 AuNP superlattice synthesis. a Scheme of superlattice preparation. First, 100 µl of AuNP@PSSH (sample details in Table 1) in toluene are pipetted onto a liquid subphase (DEG), then the well is covered with a glass slip to slow down the evaporation of the toluene. Superlattice films typically form within 16-24 h. b Photograph of a formed superlattice, scalebar 1 cm. c, d TEM measurements at different magnifications of a monolayer area in superlattices formed from AuNP25@PSSH2k (c: scalebar 500 nm, d: scalebar 100 nm). The inset in c shows the FFT of the digital image. e Low magnification of the same crystalline monolayer area covering >0.01 mm² of the TEM grid (scalebar: 50 µm). The small darker gray area in the top right corner is a bilayer. f Bilayer with few defects formed from AuNP25@PSSH5k (scalebar 500 nm). The inset shows an extended bilayer area (scalebar 100 µm). g SEM measurements of a crystalline multilayer superlattice with 22-23 layers formed from AuNP35@PSSH12k (scalebar 2 µm).

Table 1 AuNP samples used for film formation and resulting interparticle distances (gap).

| Sample name       | AuNP diameter (nm) | Ligand   | c(AuNP) (nM) | Gap (TEM) (nm) | Gap (SAXS) |
|-------------------|--------------------|----------|--------------|----------------|------------|
| AuNP25@PSSH2k     | (25.1 ± 0.7)       | PSSH2k   | 6.3          | 3.0            | 3.8 nm     |
| AuNP25@PSSH5k     | (25.1 ± 0.7)       | PSSH5k   | 29.6         | 3.3            | 4.3 nm     |
| AuNP25@PSSH12k    | (25.1 ± 0.7)       | PSSH12k  | 30.0         | 7.7            | NA         |
| AuNP35@PSSH5k     | (37.3 ± 1.2)       | PSSH5k   | 1.6          | 5.1            | NA         |
| AuNP35@PSSH12k    | (37.3 ± 1.2)       | PSSH12k  | 1.6          | 5.2            | 6.3 nm     |
| AuNP50@PSSH5k     | (50.5 ± 1.1)       | PSSH5k   | 0.7          | 1.3            | 3.6 nm     |
| AuNP50@PSSH12k    | (50.5 ± 1.1)       | PSSH12k  | 0.7          | 2.7            | NA         |
| AuNP60@PSSH2k     | (63.4 ± 1.8)       | PSSH2k   | 0.3          | 1.2            | NA         |
| AuNP60@PSSH5k     | (63.4 ± 1.8)       | PSSH5k   | 0.3          | 2.2            | NA         |
| AuNP60@PSSH12k    | (63.4 ± 1.8)       | PSSH12k  | 0.3          | 1.3            | 4.3 nm     |

*aCore diameter by TEM, with standard deviation of the mean (N > 200).

*bBy nearest neighbor analysis of TEM measurements.

*cObtained by analysis of SAXS measurements as discussed in the text.
different layer numbers within one sample are not accessible. A detailed description of the synthesis and relevant parameters is provided in the “Methods” section.

An important advantage of using grafted polymers for film formation is that they allow controlling the interparticle distance by changing their molecular weight\(^\text{10-12,39,43,56,61}\). However, although the PSSH ligand length was found to affect the interparticle distances (gaps), a clear tendency was not always observed and the correlation was not linear. For PSSH12k a correlation of gap distance with particle diameter was observed that points to the increasing attractive van-der-Waals-potentials which can be well described with scattering from a 2D-long-range periodic order within the superlattices. In comparison, the superlattice crystallinity, scanning microfocus SAXS measurements (beamsize 2.8 μm × 1.7 μm (h × v)) were performed on selected AuNP superlattice films (Fig. 2) in transmission mode. We measured SAXS patterns on hundreds of different spots on each sample including thin (monolayer and bilayer) and thick regions (multilayers). An exemplary intensity map is shown in Fig. 2a, where each pixel represents the measured intensity in a certain q-range of a single SAXS measurement. The 2D-scattering pattern and azimuthally averaged I(q) (Fig. 2b) exhibit pronounced Bragg peaks of a sixfold order which can be well described with scattering from a 2D-hexagonal lattice. This confirms the periodic order and allows extracting the lattice constant \(a\). The distributions P(\(a\)) of the lattice constant \(a\) for different samples are shown in Fig. 2c. The exceptionally narrow distributions of \(a\) underline the robust and long-range periodic order within the superlattices. In comparison, the distribution for an AuNP@Citrate-based superlattice (30 nm, functionalized with PSSH5k) is 1.5–6 times broader (Fig. 2d, gray dashed line). Remarkably, the small lattice constant difference (~0.5 nm) of AuNP25@PSSH2k and −5k due to different ligand lengths can be clearly discerned (Fig. 2c) and agrees well with the analysis of TEM measurements (Table 1).

The achieved large superlattice areas in combination with the possible deposition on transparent substrates enable the investigation of the plasmonic properties by optical microscopy and spectroscopy. The number of layers can be clearly distinguished in optical transmittance (Fig. 3a, Supplementary Fig. 14) and the layer-number-dependent optical properties can be measured with spectroscopy.

![Image](https://example.com/image)

Figure 3b shows the optical absorbance of a monolayer, bilayer, and trilayer of periodically arranged AuNPs. Pronounced absorbance peaks appear in the NIR spectral range from the direct optical excitation of plasmon polaritons that form standing waves by changing their molecular weight\(^\text{10-12,39,43,56,61}\). However, although the PSSH ligand length was found to affect the interparticle distances (gaps), a clear tendency was not always observed and the correlation was not linear. For PSSH12k a correlation of gap distance with particle diameter was observed that points to the increasing attractive van-der-Waals-potentials which can be well described with scattering from a 2D-long-range periodic order within the superlattices. In comparison, the superlattice crystallinity, scanning microfocus SAXS measurements (beamsize 2.8 μm × 1.7 μm (h × v)) were performed on selected AuNP superlattice films (Fig. 2) in transmission mode. We measured SAXS patterns on hundreds of different spots on each sample including thin (monolayer and bilayer) and thick regions (multilayers). An exemplary intensity map is shown in Fig. 2a, where each pixel represents the measured intensity in a certain q-range of a single SAXS measurement. The 2D-scattering pattern and azimuthally averaged I(q) (Fig. 2b) exhibit pronounced Bragg peaks of a sixfold order which can be well described with scattering from a 2D-hexagonal lattice. This confirms the periodic order and allows extracting the lattice constant \(a\). The distributions P(\(a\)) of the lattice constant \(a\) for different samples are shown in Fig. 2c. The exceptionally narrow distributions of \(a\) underline the robust and long-range periodic order within the superlattices. In comparison, the distribution for an AuNP@Citrate-based superlattice (30 nm, functionalized with PSSH5k) is 1.5–6 times broader (Fig. 2d, gray dashed line). Remarkably, the small lattice constant difference (~0.5 nm) of AuNP25@PSSH2k and −5k due to different ligand lengths can be clearly discerned (Fig. 2c) and agrees well with the analysis of TEM measurements (Table 1).

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Figure 3b shows the optical absorbance of a monolayer, bilayer, and trilayer of periodically arranged AuNPs. Pronounced absorbance peaks appear in the NIR spectral range from the direct optical excitation of plasmon polaritons that form standing waves in the supercrystals (see insets)\(^\text{35,36,63}\). With each additional layer a new polaritonic mode is activated, starting from a single mode for a bilayer\(^\text{35,36}\). The excitation of plasmon-polaritons leads to pronounced reflectance dips and transmittance maxima in the optical spectra (Fig. 3c). A polaritonic stop band prevents light from entering the supercrystal in the visible spectral range and light is mostly reflected\(^\text{38}\). The reflectance decreases for excitation energies larger than 2 eV because of the interband transitions of gold. The optical spectra are in good agreement with finite-difference time-domain (FDTD) simulations (compare solid and dashed lines in Fig. 3c), demonstrating the control of the structural parameters in the synthesis process. The number, energy, and spectral width of the polaritonic modes depends sensitively on the interparticle distance, number of layers, AuNP shape, diameter, and lattice type\(^\text{35,36,53,34}\). In consequence, an accurate control of all these parameters enables the design of tailored optical materials. Figure 4a shows the optical reflectance of supercrystals with different nanoparticle diameters. The polariton energies red shift with increasing nanoparticle diameter because of an increase in light–matter coupling strength\(^\text{35}\). Furthermore, the reflection dips become more pronounced because of a smaller wavelength mismatch of the light inside and outside the supercrystal. The strong dependence of the polariton energy on the nanoparticle diameter and other structural parameters implies that already slight variations within the crystal will lead to a spectral broadening or even disappearance of the polaritonic modes\(^\text{36}\). Figure 4b shows a comparison of two superlattices of similar geometry (\(d \approx 30\) nm, gaps ~3–4 nm): one prepared starting with AuNP@Citrate and the other one with AuNP@CTAC. Both were functionalized with PSSH5k, i.e. the only difference is the quality of the core AuNP.
The different uniformity and crystallinity of the two lattices is clearly visible in the spectra (Fig. 4b) and in microscope images (Fig. 4c, d). The polaritonic modes broaden or even vanish for a decreasing particle and crystalline quality.

The large transmittance of light and small interparticle gaps lead to a strong near-field intensity enhancement at the gaps between the NPs throughout the entire supercrystal. In combination with the tunability of the polaritonic excitations, this makes plasmonic supercrystals a promising platform for applications in sensing and spectroscopy. The comparison of the Raman scattering of the bulk ligand (PSSH5k) and surface-enhanced Raman-scattering (SERS) of the ligand within the superlattice hot spots yields an enhancement factor of \( \sim 3 \times 10^4 \) per molecule (Supplementary Fig. 15 and Supplementary Note 1). This stresses the potential of defined AuNP superlattices for SERS and related techniques like surface-enhanced infrared-absorption (SEIRA) spectroscopy in addition to the design of polaritonic materials.

**Discussion**

Large AuNP-supercrystals with hexagonal order ranging from 2D to 3D, i.e. monolayer to multilayer, were synthesized with straightforward protocols. By varying particle diameter and concentration, as well as ligand length and evaporation time, large AuNP-supercrystal sheets were synthesized with varying number of layers and interparticle distances in the range of 1–8 nm. Since PSSH-thiol ligands are available with almost arbitrary molecular weights, larger gaps should be possible as well, but for strong plasmonic coupling small gaps are preferable. The obtained large scales in combination with the high degree of periodic order allow

$$\text{the formation of periodically coupled plasmon-polariton modes, pointing towards applications in optical metamaterials and surface-enhanced spectroscopies. More complex superlattices (e.g. binary and including NP of different materials) can be envisaged depending on the desired application. A key point for utilizing the protocol for different NP materials and shapes will be the particle quality and a controlled surface chemistry. A complete ligand exchange and thorough purification should provide stable dispersions of the according nanomaterial in suitable solvents without additional stabilizers and at sufficiently high concentrations. The correlations of geometry and electronic and/or mechanical properties would be interesting to address in future studies. Wang et al. recently presented organic nano-floating-gate memory devices based on self-assembled AuNP-films, which greatly benefit from defined ordered structures compared to amorphous films. This can reasonably be expected to be the case for many other microelectronic devices. Thus, the potential for fundamental studies with well-defined superlattice structures is quite broad. Our protocol expands the available range of precise geometries for such studies. It demonstrates that self-assembled structures obtained by wet-chemistry can compete with lithographic precision and control, and probably also provide sufficiently large areas for various devices and applications in the near future.}$$

**Methods**

**Materials.** Tetrachloroauric(III) acid (≥99.9% trace metals basis), hexadecyltrimethylammonium bromide (CTAB, ≥98%) and chloride (CTAC, ≥98%), L-ascorbic acid (reagent grade) and sodium borohydride (≥98%) were from Sigma-Aldrich (USA). Toluene (≥99.5%), tetrahydrofuran (≥99.5%), and ethanol (denat., >96%) were from VWR (USA). DEG (reagent grade) was from Merck (Germany). Thiolated polystyrenes (PSSH, PSSH2k: \( M_w = 2000 \) g mol\(^{-1}\), \( M_n = 2300 \) g mol\(^{-1}\); PSSH5k: \( M_w = 5300 \) g mol\(^{-1}\), \( M_n = 5800 \) g mol\(^{-1}\); PSSH10k: \( M_n = 11,500 \) g mol\(^{-1}\),
\[ M_w = 12,400 \text{ g mol}^{-1} \] were from Polymer Source (Canada). All reagents were used without further treatment.

**AuNP@CTAC synthesis.** Gold nanoparticles (AuNP) were synthesized based on the protocol presented by Zheng et al. \(^5^5\) that was upscaled to achieve sufficiently high AuNP concentrations. All solutions were in ultrapure water form (18.2 \( \Omega \)). For the initial CTAB-stabilized seeds, sodium borohydride (NaBH\(_4\), 600 \( \mu \)l, 10 mM) was quickly injected into a mixture of CTAB (9.9 ml, 100 mM) and tetrachloroauric (III) acid (HAuCl\(_4\), 100 \( \mu \)l, 25 mM) under rapid stirring (1000 rpm) and then stirred at 300 rpm for 3 min. Afterwards, the reaction mixture was left for 3 h without agitation.

**First growth step:** 50 \( \mu \)l of these CTAB-seeds were mixed with ascorbic acid (1.5 ml, 100 mM) and CTAC (2.0 ml, 200 mM) at 600 rpm, followed by a one-shot-injection of HAuCl\(_4\) (2.0 ml, 0.5 mM). After 15 min stirring (300 rpm), the AuNP were purified by centrifugation (20,000 \( \times \) \( g \) \times 20 min) and the pellet redispersed in CTAC (1.0 ml, 20 mM). For an upscaled version of this first growth step, all volumes were scaled up by a factor of 10 without any other changes to the protocol. These AuNP@CTAC were used as seeds to synthesize all AuNP@CTAC with larger diameters. To this end the AuNP@CTAC were purified by two additional centrifugation steps, without changing the AuNP and CTAC concentrations, i.e. the pellets were redispersed in 20 mM CTAC.

**Second growth step:** CTAC (20 ml, 100 mM) and the desired volume of AuNP@CTAC seeds (in 20 mM CTAC) were mixed and treated with ultrasound for 10 min. The mixture was then stirred (400 rpm) in a water bath at 30 °C, ascorbic acid (1.3 ml, 10 mM) was added and after one minute the addition of

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1.0 1.5 2.0

\[ 100 \text{ nm} \]

\[ \text{Reflectance (%)} \]

0 50 100 150 200

\[ 50 \text{ nm} \]

\[ 63 \text{ nm} \]

\[ \text{Excitation energy (eV)} \]

1.2 1.6 2.0

\[ 1000 900 800 700 600 \]

\[ \text{Wavelength (nm)} \]

20 40 60 80

\[ \text{Reflectance (%)} \]

CTAC

Citrate

\[ \text{Wavelength (nm)} \]

1500 1200 900 600

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HAuCl₄ (20 ml, 0.5 mM) with a syringe pump at 20 ml h⁻¹ was started. After the addition completed, the mixture was stirred (400 rpm) for another 10 min at 30 °C and then the AuNP@CTAC solution was centrifuged 2000 rpm for 30 min to remove the supernatant. The AuNP@CTAC stock was prepared with 1.6 ml of water. The parameters of the AuNP@CTAC seeds were estimated with the absorbance at 400 and 450 nm. The AuNP concentrations were estimated with the absorbance at 400 and 450 nm. The AuNP concentration did not sensitively affect the outcome of the self-assembly experiments. As a tendency, higher particle numbers lead to thicker crystals. A smaller number of defects upon slow evaporation favors thicker crystals. A longer evaporation time can be achieved by covering the liquid interface with water. The parameters of the AuNP@CTAC seeds (added volume 200 μl, diameter dSEP, and seed concentration cSEP) used for the different samples are presented in Table 1. The data that support the findings of this study are available from the corresponding author upon reasonable request.

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**Small-angle X-ray scattering.** The SAXS experiments were performed at beamline P10 at PETRA III (DESY, Hamburg). An X-ray photon energy of E = 8 keV was used. The X-ray beam was focused by compound refractive lenses to 2.8 μm × 1.7 μm (f × s). The detector (Dectris Eiger X 4M) was placed 5 m downstream of the sample, covering a q-range from 0.014 to 1.15 nm⁻¹. The samples were mounted in a vacuum chamber connected to an evacuated flight path. SAXS patterns were taken from different regions of the samples in scanning mode. Therein, scanning steps of 5–10 μm step size were typically chosen in horizontal and vertical directions normal to the X-ray path. At least 2000 individual patterns were measured from each sample in this way, obtaining >700 hits that were used for further analysis (cf. Fig. 2a: some measurements just cover TEM-grid without sample). From the patterns, the lattice constants a were obtained from the position of the indexed Bragg reflections. The distributions P(a) were calculated from the histograms of a. The interparticles distances (gaps) based on SAXS (cf. Table 1) were determined by subtracting the AuNP diameters from particle form factor fits from the lattice parameters a.

**Optical microscopy.** The optical spectra of the gold nanoparticle trilayer were recorded with a home-build micro-absorbance spectrometer. Details of the setup can be found in ref. 36. A supercontinuum laser (Fianium, SC-400-4) was used as a white light source. The light was guided through a linear polarizer into an inverted optical microscope (Olympus, IX71) and focused with an x100 objective (Leica HCX PL Fluotar x100) onto the sample. We used objectives with a numerical aperture N.A. = 0.9 to focus light to a diffraction-limited spot on the sample. This corresponds to a maximum angle of incidence of 64° outside the supercrystal. The maximum angle of incidence inside the supercrystal is with 5–13°, much smaller and close to normal incidence because of the large effective index of refraction, nₑ = 4–10, of the supercrystals (35). The laser power was kept below 200 μW. The AuNP films were transferred to a glass substrate for optical characterization. The layer number was identified through the optical contrast in transmission (cf. Supplemental Fig. 14). The sample was moved in x-direction and y-direction with a combination of a motorized stage and a piezo stage. The transmitted light was collected with a second x100 objective (Olympus MPlan FL N BD x100) and coupled through a fiber (Ocean Optics, QM600-2-UV-BX for 450–900 nm and BF600–VIS–NIR for 900–1600 nm) into a spectrometer (AvaSpec, AvaSpec3648 for 450–900 nm and AvaSpec NIR512 for 900–1600 nm). In a subsequent measurement, the back-reflected light was separated from the incoming light beam with a beam splitter (ThorLabs, BS250R for 450–900 nm and BS290R for 900–1600 nm) and detected with the same combination of fibers and spectrometers as for the transmitted light. The spectra of the VIS and NIR ranges were pinned together.

**Finite-difference in the time-domain (FDTD) simulations.** For the FDTD simulations in Fig. 3 the commercial software package Numerical FDTD Solutions was used as described recently (36,37). Spherical NPs with 50 nm diameter were packed into a hexagonal lattice with 1.6 nm interparticle gaps. Three layers were stacked by the x-f is sequence of FDTD crystals to construct a trilayer. A mesh oversampling region with 0.5 nm cell was used to resolve the geometry of the supercrystal. The dielectric function of gold was modeled by fitting experimental data from Olmon et al. (37) and the polystyrene ligand molecules were modeled as a dielectric medium with refractive index n = 1.4 filling the space between the NPs. The FDTD simulation region was chosen as the unit cell of the supercrystal with periodic boundary conditions along x and y. Perfectly matched layers were used along z. Light was injected along z with a broadband plane wave source. The transmittance and reflectance were recorded with power monitors behind the nanoparticle layers and behind the source.

**Data availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.
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Author contributions
F.S. developed the synthesis protocol. F.S. and O.P. synthesized AuNP and AuNP superlattices. F.S. did the TEM measurements, F.S. and O.P. analyzed the TEM data, F.S., F.L., and F.W. performed the SAXS measurements, F.L. and F.W. analyzed the SAXS data. N.S.M. and Y.O. did the optical measurements and calculations including SERS. F.S., H.L., and S.R. supervised the project. All authors discussed the results and implications and commented on the manuscript at all stages. F.S. and H.L. wrote the manuscript with contributions of all authors. All authors have given approval to the final version of the manuscript.

Competing interests
The authors declare no competing interests.

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