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Design, Self-Assembly, and Switchable Wettability in Hydrophobic, Hydrophilic, and Janus Dendritic Ligand-Gold Nanoparticle Hybrid Materials

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ABSTRACT: Controlling nanoparticles' (NPs) surface polarity, colloidal stability, and self-assembly into well-defined complex architectures is of paramount importance for emergent nano- and biotechnologies, and each depends strongly on the ligand shell composition and chemical nature. In this study, a series of dendritic ligands with hydrophobic, hydrophilic and Janus surface groups were synthesized, grafted onto Au NPs, and their effects on the self-assembly behavior and the surface polarity of the corresponding hybrid materials were investigated. The ligand synthesis utilized a generalized, flexible strategy that independently introduces dendritic end groups, responsible for the surface polarity and colloidal properties, and specific surface NPs binding groups, reducing the number of synthetic steps. The dendritic ligands obtained were grafted onto NP surfaces through solution phase ligand-exchange, and the resulting NP-dendron hybrids were studied using a variety of techniques such as transmission electron microscopy (TEM), UV-vis, and small-angle X-ray scattering (SAXS). By controlling the solvent evaporation rate during self-assembly, these dendronized Au hybrids self-organize into highly ordered thin films comprised of close-packed arrays of NPs, where the interparticle separation can be varied as a function of the dendritic generation and end group chemistry. Moreover, contact angle and colloidal observations revealed the strong dependence of the dendron end-group and generation on the NP surface polarity is dependent on solvent exposure, revealing a surface polarity memory effect, making this material a model system for surfaces that demonstrate switchable wettability.

Introduction

The study of coordination and self-assembly behavior of ligands on nanoparticle (NP) surfaces is of critical importance as it provides the key to understanding and engineering properties such as colloidal stability,^{1,2} electronic conduction,³ magnetic and optical properties,⁴⁻⁶ and biological/catalytic activity.⁷⁻¹¹ For as-synthesized NPs, the nature of the ligands coating NP surfaces depends on the specific synthetic methods employed. For those synthesized in organic media, capping ligands are usually selected from commercially available alkyl-containing molecules that have either acid, amine, phosphine, or thiol surface binding groups.^{12,13} By contrast, in aqueous media, syntheses of NPs involve polar ligands such as ascorbic acid, citric acid, or polyethylene glycol derived molecules.14-17 Ligands with specific properties are often attached to the NP surface by post-synthetic surface modification (ligand exchange) or functionalization of the ligand shell.^{18,19} To this end, many different types of ligands such as polymeric,^{20–23} dendritic,^{24–29} liquid crystalline,^{30–35} and small molecules^{2,36} have been grafted on NP surfaces to introduce solubility, steric, biological, sensing, optical, magnetic, and electronic properties.



Figure 1. Various examples of surface functionality engineering.





^aReagents and conditions: (i) K_2CO_3 , KI, DMF, 80 °C, 12h; (ii) LiAlH₄, THF, 60 °C, 3h; (iii) KOH, THF/H₂O/MeOH, 4h, 80 °C for 4 and 13, 4h at 50 °C for 5, 14, and 18; (iv) SOCl₂, CH₂CL₂, 3h, rt; (v) 1 equiv. of 8, K_2CO_3 , KI, DMF, 85 °C, 12h.

In most cases, the chemical nature of the ligands is limited to being either hydrophilic, introducing aqueous compatibility, or hydrophobic, giving rise to dispersibility in organic solvents of the corresponding hybrids (Figure 1a). A limited number of ligands reported to date have a dual nature, i.e. contain both hydrophobic and hydrophilic moieties.³⁷ Amongst those described in the literature are diblock copolymer based ligands (Figure 1b) that create a double corona around the NP, where only one block fragment is on the periphery and has the largest effect on the final colloidal properties. There are a limited number of examples using amphiphilic block copolymers where both blocks interact with the surrounding solvent, as these have to include a "v-shaped" junction.³⁸⁻⁴⁰

A selection of these amphiphilic ligands exhibit switchable wettability properties, where the polarity of the surface of the material can be changed by exposing the system to various stimulants, such as a variety of solvents.^{41,42} The ability to adjust the wettability properties of a surface is of particular value due to the applications of these materials for smart surfaces, such as self-cleaning surfaces, 43,44 and nanofabrication templates with switchable morphologies. 45

Amongst other possible ligand architectures, dendritic ligands have unique advantages. They provide a well-controlled synthetic platform where, the ligand bulkiness and the nature and polyvalency of the endgroups can be tuned independently from each other.^{46,47} These properties make them an attractive system for NP surface functionalization and to date they have found utility in NP synthesis⁴⁸ as well as optical,^{26,49} magnetic,²⁷ biological,⁵⁰ colloidal,⁵¹ self-assembly,^{26,52} and catalytic¹⁷ property modification.

However, in reported examples, the chemical nature of the dendritic ligands is limited to being either hydrophilic, or hydrophobic, (Figure 1c). Although, Janus dendrimers are well known nanostructures,⁵⁰ to the best of our knowledge, there is no literature report that describes Janus dendrons as NP ligands where both hydrophilic and hydrophobic moieties are positioned at the terminal part of the ligand (Figure 1d), and therefore are in direct contact with the solvent and actively contribute to the hybrid surface polarity.

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Scheme 2. The synthesis of disulfide dendrons 22-26^a



^aReagents and conditions: (i) SOCl₂, CH₂Cl₂, rt, 3h for 10, 11, 19, and oxalyl chloride, 2,6-ditert butyl 4-methyl pyridine, CH₂Cl₂, rt, 3h for 15 and 16, then 20, Et₃N, DMAP, CH₂Cl₂, -10°C \rightarrow rt, 12h; (ii) I₂, CH₂Cl₂, rt, 12h.

Of relevance to the Janus dendritic ligands are NPs that have Janus character obtained by templating two different ligands onto the surface of the NP.⁵³ This strategy leads to phase separation on the NP surface into vast regions of either hydrophobic and hydrophilic character, where by comparison, a dendritic Janus molecule will cover the NP surface homogeneously, and the two distinct moieties will not be able to separate into large domains of different nature.

Herein, we present an efficient synthesis of a library of monodisperse dendritic ligands capable of tuning NP surface polarity.
Hydrophobic, hydrophilic, and Janus ligands presented here allow simple solution phase ligand exchange and produce uniform coverage where the organic shell polarity is determined by the nature of the corresponding ligand end-group.

Hydrophobicity and hydrophilicity are engineered using dendritic systems containing dodecyl and triethylene glycol methyl ether moieties, respectively. The increase in the number of these groups as a function of the generation provides subsequent advancement of polarity, i.e. a higher generation dendron with polar end-groups becomes more hydrophilic and similarly a higher generation dendron with nonpolar end-groups becomes more hydrophobic. The Janus dendritic ligand is designed to contain covalently linked polar and nonpolar groups positioned at the periphery of the dendron, which enables modulation of the polarity in between the systems with opposite polarity, that can be further tuned through exposure to various solvents where a solvent dependent memory effect phenomenon is revealed. **Results and Discussion**

Ligand Design and Synthesis. To study the influence of dendritic ligands, we designed a molecular system where the surface anchoring unit (disulfide-based functional group) is located at the apex and either or both hydrophobic and hydrophilic moieties are covalently mounted on the terminal part of the Frechet type dendron.⁵⁴ This approach gives efficient access to the desired dendrons where the hydrophobic, hydrophilic, or Janus moieties are present at the periphery, allowing them to directly interact with each other as well as with the surrounding media, precisely tuning polarity and solubility properties. To study the effects of the ligand shell polarity as a function of the dendritic generation, first and second generation hydrophobic and hydrophilic dendrons were synthesized, and the Janus dendron (a second generation dendron) was synthesized containing a 1:1 molar ratio of hydrophobic/hydrophilic moieties to be intermediate to the hydrophobic and hydrophilic ligands. The synthesis of the targeted ligands was started by reacting readily available methyl gallate (methyl 3,4,5-trihydroxybenzoate 1) with dodecyl bromide or triethylene glycol methyl benzenesulfonate using Williamson etherification under mild basic conditions (Scheme 1a).^{55–57} Reduction of the methyl ester function of 4 and 5 into benzyl alcohols 6 and 7 and subsequent chlorination using thionyl chloride gave access to the valuable chlorinated intermediates 8 and 9 that are required to build the higher generation ligands. The common intermediates 4 and 5 were hydrolyzed to give acids 10 and 11 that are necessary for building the first generation hydrophobic and hydrophilic



Figure 2. Representative TEM micrographs of self-assembled NP films of (a) as-synthesized Au@Olam, (b) Au@22, (c) Au@23, (d) Au@24, (e) Au@25, and (f) Au@26 ($\phi_{Au} \approx 7.6 \pm 0.5 \text{ nm}$).

dendrons (Scheme 1a). Higher generation dendrons were synthesized in very good yields (ca. 90%) by reacting methyl 3,5dihydroxybenzoate, **12**, with two equivalents of **8** or **9** by Williamson etherification, followed by the hydrolysis of the methyl ester function to give corresponding acids **15** and **16** with nonpolar and polar end-groups, respectively (Scheme 1b). For the synthesis of the Janus building blocks, the introduction of both nonpolar and polar end-groups was carried out in a stepwise fashion to ensure the precise end-group control. Thus, etherification of methyl 3,5-dihydroxybenzoate **12** with one equivalent of nonpolar building block **8** gave access to the intermediary monofunctionalized benzoate **17**, which was further reacted with one equivalent of polar building block **9** to yield the Janus ester **18**; the latter was hydrolyzed quantitatively to the corresponding Janus acid **19** (Scheme 1c).

Finally, the targeted disulfide dendrons were synthesized by an esterification reaction between the various dendritic acids 10, 11, 15, 16, 19 and disulphide-bearing molecule 21. The synthesis was carried out in a one-pot two-step process where acid chlorides were first generated *in situ* from carboxylic acids and then reacted with alcohol 21. Scheme 2 shows the synthesis of dendrons 22-26 while all additional synthetic details are provided in Supplementary Information. The resulting library is designed to give the opportunity to study the effects of i) the polarity of the ligands within identical generation, and of ii) the dendritic generation on the colloidal stability and self-assembly of the corresponding dendronized Au hybrids.

Ligand Exchange with Gold NPs and Self-Assembly. To explore how various dendritic ligands affect a variety of properties of NPs, each dendrimer was grafted onto Au NPs, with diameters $\phi_{Au} \approx 5.2 \pm 0.5$, 7.6 ± 0.5 and 10.2 ± 0.6 nm, respectively, using a solution phase ligand-exchange procedure which is known to afford uniform dendritic surface coverage²⁶ (final NP-dendron hybrid materials will therefater be denoted as Au@dendron). A solution of oleylamine (Olam) stabilized as-synthesized Au NPs (Au@Olam) were mixed with an excess of the dendritic ligand (**22-26**) and stirred at room temperature to allow the exchange of the Olam ligands with the disulfide dendrons. After 1 h, the hybrids were precipitated out using an antisolvent (methanol for materials with ligands 22, 23, and 24, and toluene for those with ligands 25 and 26) and the precipitate was collected by centrifugation. This step was repeated 3 times to ensure the complete removal of any excess unbound ligands (dendrons and Olam).

During surface ligand exchange process, the dendritic ligands were introduced into the organic shell without affecting the size of the inorganic core of the material. TEM analysis of the NP size distribution before (Au@Olam) and after ligand exchange (Au@dendron) shows no difference in average diameter of the core (Figure S1d), also in agreement with UV-vis measurements (Figure S1b). The ligand exchange process was monitored a posteriori by measuring the interparticle distance of resulting hybrids in self-assembled monolayers (TEM). A prolonged reaction time did not yield any variation in the spacing, leading us to believe that the NP surface had reached saturation with the dendrons. This exchange was additionally confirmed with Nuclear Magnetic Resonance (NMR) spectroscopy analysis of Au NPs before and after the ligand exchange, as shown in Figure S2. The disappearance of the oleylamine olefinic hydrogen signals at 5.3-5.4 ppm and appearance of dendron signals at 4, 5, and 6.6 ppm clearly indicate the successful exchange. Thermogravimetric analysis was performed on a representative sample of the hybrid material (Au@22, $\phi_{Au} \approx 5.2 \pm 0.5$) to determine the grafting density of ligands per NP surface unit (Figure S3), which was found to be in good agreement with previous studies using similarly sized Au NPs.²⁶

The end-group nature and the generation of the ligands are important parameters controlling the surface polarity and colloidal properties of the final Au@dendron hybrid materials. Ligands with the hydrophobic end-groups 22 and 23 are expected to have lower affinity for polar solvents compared to their PEG based analogs 25 and 26, while the Janus ligand 24 is expected to lie in-between. The change of surface polarity was studied using contact angle measurements of self-assembled superlattice films and solubility studies.

The Au@dendron hybrids, Au@22, Au@23, and Au@24 were induced to self-assemble into thin films on liquid-air interface, following a previously reported procedure.⁵⁸ A diluted solution

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of Au@dendron hybrids in hexanes was deposited on a polar subphase of diethylene glycol (DEG) and allowed to evaporate slowly, resulting in floating NP films. This method only works for hybrids whose ligand shell is dominated by nonpolar character and therefore they dissolve in hexane layer and remain on the interface after solvent evaporation. Under these conditions, polar hybrids such as Au@25 and Au@26, have revealed higher affinity for the subphase and failed to remain on the interface. Therefore, the self-assembled monolayers of these polar systems were produced on a solid-air interface, where colloidal solutions in chloroform were dropcast on TEM grids and dried slowly in a partially enclosed chamber. In all cases, the thickness of the self-assembled film was controlled by the concentration of NPs and the amount of the initial solution. This set of ligands allow NPs to self-assemble into highly ordered colloidal crystalline films. Figure 2 shows TEM images of ordered monolayers obtained from Au@Olam 7.6 \pm 0.5 nm NPs, as well as films obtained from same batch of NPs coated with dendritic ligands 22-26.



Figure 3. Contact angle measurements: images showing water droplets cast onto films of (a, b, and c) Au@23, (d, e, and f) Au@26, (g, h, and i) Au@24 ($\phi_{Au} \approx 7.6 \pm 0.5$ nm) after treatment with hexanes (a, d, g), CHCl₃ (b, e, and h), or MeOH (c, f, and i).

The wettability of the hybrids was evaluated by contact angle measurements, using the static sessile drop method, performed with a water droplet cast on Au@dendron films, deposited on a glass substrate. These films were multiple layers thick, as they were also used for SAXS and UV-vis studies, negating any substrate surface effects. Hydrophobic hybrids, Au@22 and Au@23, show large contact angles $(79 \pm 5^{\circ} \text{ and } 83 \pm 6^{\circ}, \text{ respec-}$ tively, Figure 3, S4b, Table 1), whereas for their hydrophilic analogs, Au@25 and Au@26, much smaller angles $(57 \pm 3^{\circ})$ and $50 \pm 5^{\circ}$) were observed. This is in good agreement with what should be expected, as high surface polarity should result in increased wettability and therefore evidenced by the spreading of the water droplet on the films, and thus, with smaller contact angles. The Janus dendron based-hybrid system, Au@24, shows a contact angle of $65 \pm 2^{\circ}$ that is intermediate compared to the polar and nonpolar systems, reflecting the 1:1 molar ratio of hydrophobic and hydrophilic moieties present at the periphery of the dendritic molecule, and therefore the homogeneous distribution of both polar and nonpolar segments within the NP

ligand shell. This demonstrates the precise tuning of the NP surface polarity and wettability by adapting the chemical nature of the ligand end-groups and dendritic generation.

Interestingly, the contact angle measurements done after exposure to various solvents revealed a surface polarity memory effect that is present only in case of the hybrid material containing the Janus ligand. As shown in Figure 3, the hybrid materials with either hydrophobic or hydrophilic character, Au@23 and Au(a)26, show no changes in the contact angle after exposure to solvents with very different polarity such as MeOH and hexanes. Conversely, Au@24 exhibits hysteresis, where the polarity of the surface can be controlled by exposing the film to either one of these solvents, as seen by the contact angle changing from 76 \pm 3° to 60 \pm 3°, respectively, shown in Figure 3 and Table 1. The original contact angle of $65 \pm 2^{\circ}$ is consistent with our findings, as the Janus material in that case was exposed to CHCl₃, which has an intermediate polarity compared to hexanes and MeOH. This switchable wettability property is due to the presence of both a hydrophilic and hydrophobic arm on the dendron, where the presence of a polar solvent will change the structural conformation of the material, possibly by backfolding the nonpolar dodecyl based arms, allowing the surface to be dominated by the polar triethylene glycol arms similar to the phenomenon observed previously on V-shaped polymers.^{40,41} The opposite of this is true when nonpolar solvent such as hexanes is used. This unique property makes the Au@24 hybrid material a model system for controlled surface wetting. While this hybrid material was tested as a smooth surface, we expect that this property would be amplified if the material was deposited onto a rough surface.



Figure 4. Dispersibility of Au@dendron hybrids in (top row) hexane/water, and (bottom row) water/chloroform mixtures: (a and d) Au@22, (b and e) Au@24, (c and f) Au@25 ($\phi_{Au} \approx 7.6 \pm 0.5$ nm).

Ligand polarity is also reflected in the colloidal properties of the hybrid systems, as seen in Figure 4 and Table S1. Shells of nonpolar 1st and 2nd generation ligands **22** and **23** behave similarly, and allow dispersibility of the corresponding hydrophobic hybrids in nonpolar organic solvents such as hexanes and toluene. Conversely, ethylene glycol based end-groups introduce a polar shell, and thus the corresponding hybrid systems gain dispersibility in polar solvents such as methanol and water. Interestingly, all ligands synthesized here have affinity towards polar aprotic solvents with medium dielectric constants like THF

Table 1.	Structural,	plasmonic,	and polarit	y properties o	f the Au@dendron	hybrids.
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	Edge-to-edge separation (nm) measured on different size NPs			$\lambda_{max} (nm) \ (films)^{*}$	Contact Angle (°), measured after exposure to different solvents [*]		
	5.2 ± 0.5 nm NPs	7.6 ± 0.5 nm NPs	10.2 ± 0.6 nm NPs		Hexanes	CHCl ₃	МеОН
Au@Olam	3.3**	2.4	1.3	596	-	71 ± 2	-
Au@24	4.7	4.4	3.9	550	76 ± 3	65 ± 2	60 ± 3
Au@22	4.3	3.5	2.5	547	-	79 ± 5	-
Au@23	5.4	5.6	5.2	544	79 ± 4	83 ± 6	80 ± 2
Au@25	-	-	-	-	-	57 ± 3	-
Au@26	-	5.1	-	557	48 ± 1	50 ± 5	48 ± 2

Measurements taken using samples $\phi_{Au} \approx 7.6 \pm 0.5$ nm, **Measurement taken from as-synthesized NPs 5.6 \pm 0.5 nm in size.



Figure 5. Superlattice monolayers of various dendron coated NPs: Au@22 a) 5.2 ± 0.5 nm, b) 7.6 ± 0.5 nm, and c) 10.2 ± 0.6 nm Au NPs; Au@23 d) 5.2 ± 0.5 nm, e) 7.6 ± 0.5 nm, and f) 10.2 ± 0.6 nm Au NPs; Janus Au@24 g) 5.2 ± 0.5 nm, h) 7.6 ± 0.5 nm, and i) 10.2 ± 0.6 nm Au NPs; Janus Au@24 g) 5.2 ± 0.5 nm, h) 7.6 ± 0.5 nm, and i) 10.2 ± 0.6 nm Au NPs and Au@Olam j) 5.6 ± 0.5 nm, k) 7.6 ± 0.5 nm, and l) 10.2 ± 0.6 nm Au NPs. A low m) and high resolution n) hexagonal double layer and o) *fcc* assembly of Au@23 coated 10.2 ± 0.6 nm Au NPs.

and EtOAc, and all hybrid systems tested here including Au@Olam are dispersible in CHCl₃ (Table S1). When the hybrids are suspended on an interface of the immiscible solvent combination of water and chloroform, they do not always prefer to be suspended into the solvent of matching polarity. For example, hybrids with polar ligands, Au@25 and Au@26, are readily water soluble, but remain in chloroform when dispersed in water/chloroform mixture, an example of which is shown in Figure 4. This can be attributed to the presence of triethylene glycol methyl ether units that appear to be sufficient for water solubility, but the presence of nonpolar parts such as linear

alkyl (undecyl) chain and benzene ring would have undoubtedly increased the overall lipophilicity of the system to support its higher affinity towards chloroform. This can be especially important for applications where liquid-liquid extraction is a purification or an isolation step.

Dendronized NPs were found to assemble into close-packed colloidal crystalline film structures where the interparticle spacings are controlled by the generation of the ligand, as previously demonstrated,^{26,59} but also by the amphiphilic nature of the endgroups, as well as the size of the inorganic core. To explore this phenomenon further, we studied every possible combination

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made of three different sizes ($\phi_{Au} \sim 5.2 \pm 0.5$ nm, 7.6 ± 0.5 nm and 10.2 ± 0.6 nm) of Au NPs with three different ligands 22-24, as well as with Olam as reference compounds. Information about interparticle spacings was derived from TEM images and further confirmed by small-angle selected area electron diffraction (SAED) patterns of well-ordered superlattices assembled on liquid-air interface (Figure 5a-l and S5). From the small-angle SAED patterns (Figure S5), the distance from the center of an outer spot to the center of the opposite outer spot was measured, and divided by 2 to provide the radius, r, and this distance was converted from pixels to nanometers. Then, using 10 the relationship $d = \frac{\lambda L}{r}$, where λ is the electron wavelength and 11 L is the distance of the sample from the screen, the interplanar 12 13 distance, d, was calculated and converted into interparticle dis-14 tance.

Figure 5a-l shows the superlattice films of all 12 combinations. The resulting interparticle separations are reported in Table 1. For every hybrid tested, the edge-to-edge separation increases as expected with the ligand size, but this separation is the largest when they are placed on the smallest NPs (5.2 ± 0.5 nm) and the smallest when they are placed on the largest NPs (10.2 ± 0.6 nm). This trend is clearly visible when plotting edge-to-edge separations against ligand molecular weights (Figure 6a) for the 3 NPs diameters. Additionally, the larger ligand (23) seems to counterbalance this tendency more effectively than their smaller analogs and appears less sensitive to NP diameter variations as seen when plotting edge-to-edge separations against NP core diameters (Figure 6b). This seems to indicate that during superlattice films formation, the soft and deformable ligand shell is slightly compressed by interparticle attractive forces (Au cores are incompressible), which are stronger for larger particles.^{60,61} The softness of the ligand shell is dependent on the coverage density which varies as a function of NP diameter (number of ligands per nm^2 of the NP surface). Due to the larger curvature (c = $2/\phi_{Au}$) of the small NPs, larger free volume is generated, allowing ligands to accommodate more easily at the NP surface, yielding thus a more efficient ligand packing. Hybrids with ligands 22 and 24 follow this trend as well, but the slope is less pronounced as for Olam, confirming a slight coarsening of the ligand shell upon ligand size increase.



Figure 6. Edge-to-edge separation dependence on a) ligand molecular weight, and b) NP core size, where dotted lines represent calculations from SAED patterns.

Small-angle SAED of ligands 22 and 23 (Figure S5), the largest and smallest synthesized ligands, was employed to confirm this trend and the results are included in Figure 6b. This observation indicates that large bulky ligands counterbalance the interparticle attraction forces more than smaller ligands, and is in good agreement with earlier work where the ligand linear contraction and deformation are found to be the smallest for higher generation dendrons (reinforcement of the rigidity).⁶² Although, due to the different ligand architecture reported here, a direct comparison to the literature is difficult.

The crystalline nature and the modulation of interparticle spacing of the self-assembled films in selected examples were further confirmed by the small-angle X-ray scattering (SAXS) and UV-Vis absorption, shown in Figure S1. In SAXS (Figure S1c), performed on films made from dendron coated 7.6 ± 0.5 nm NPs, the maximum of the first reflection peak of the NPdendron hybrids shifted from $q = 0.0705 \text{ Å}^{-1}$ for the as-synthe-



Figure 7. Various Moiré patterns in dendron 23 coated 10.2 ± 0.6 nm (a-c and e) and 5.2 ± 0.5 nm (d and f) Au NPs.

-sized Au@Olam to $q = 0.0585 \text{ Å}^{-1}$ for Au@24, indicating an overall increase in separation from 1.7 nm to 3.7 nm, respectively. The slight discrepancies with the values reported in Table 1 are possibly due to the thickness of the NP films, as it has been previously reported that an increase in film thickness can result in a change in the superlattice structure, which requires further analysis outside the scope of this study.⁶³ All the samples, except for Au@25, showed an additional diffuse reflection, and together, these two diffraction signals correspond to the reflections of a hexagonal lattice. In the case of Au@25, self-assembly was not observed in TEM, which is consistent with the absence of any reflection peaks from SAXS.

In solution phase UV-Vis measurements (Figure S1b), all the NPs with the various ligands on their surface have the same maximum absorption wavelength ($\lambda_{max} = 540$ nm), which indicates that the ligand exchange does not alter the size and shape uniformity of the NPs. This is in good agreement with the size distributions of the same NP samples measured from their TEM images (Figure S1d). When the samples are assembled into thin films, the plasmon resonance shows a red shift from the solution spectra. The shift is maximum for as-synthesized particles and decreases as a function of increasing interparticle separation reaching a minimum value in case of the largest ligand 23 (Table 1). The observed trend in this shift is caused by changing the average dielectric constant of the surroundings of the NPs, and the distance dependent interparticle coupling which is consistent to the trend observed previously.²⁰

Chemistry of Materials

Additionally, 7.6 ± 0.5 nm Au NPs with 22 on the surface were mixed with Au@23, as well as Au@24, to obtain binary mixtures, which are shown in Figure S7. These mixtures also form superlattice films, where the edge-to-edge spacings of 4.4 nm for Au@22 mixed with Au@23, and 3.7 for Au@22 mixed with Au@24, are intermediate compared to the single component superlattices.

During liquid-air interface self-assembly, the film thickness is controlled by the amount and the concentration of NP containing solution. While interparticle spacings are measured on single layered areas, well-ordered multilayers can also be obtained. In Figures 5m,n we show TEM images of low and high resolution of hexagonal close-packed *hcp* bilayer superlattices which, together with single layered domains, dominate the entire sample. However, in some rare cases, other structures such as *fcc* (Figure 50) can also be found.

Further TEM analysis of Au@dendron hybrid films reveal a range of different Moiré patterns that arise from misalignment of ordered layers.⁶⁴ Figures 7a-f shows TEM images of bilayer or trilayer films where at least one layer is rotated by a certain degree in relation to another. Thus, repeating hexagonal motifs are revealed, the size of which has an inverse relationship with the misalignment degree.⁶⁵ Figures 7a,b show two ordered layers of dendron 23 coated 10.2 ± 0.6 nm Au NPs offset by ~5° and ~9° resulting in hexagonal motifs that have a center to center distance of 160 and 80 nm. Larger rotation angles cause the motifs to decrease in size and at ~30° it starts to resemble 12fold order found in quasicrystals (Figures 7c,d and Figure S6).^{60,65–67} Three layered misaligned structures are more complex, as seen with examples of dendron 23 coated 10.2 ± 0.6 nm (Figure 7e) and dendron 23 coated 5.2 ± 0.5 nm Au NPs (Figure 7f), where both are thought to arise from $\sim 20^{\circ}$ rotation of one layer with respect to hcp bilayer. In some cases, the variety of Moiré patterns could be found in a close proximity to each other allowing them to be imaged in a single TEM image (Figure S8). Interestingly, these well-defined patterns were more prominent in samples where largest dendritic ligand 23 was used however, more research is needed to identify the ligand size dependence on layer to layer misalignment.

Conclusion.

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We have demonstrated a highly flexible and efficient route to synthesize novel dendritic ligands with tunable surface polarity. The polarity is controlled by the number and nature of dendron end-groups and allows the NPs to be dispersed in a wide variety of solvents. Moreover, the Janus ligand featuring structurally well-defined end-groups of opposite polarity both located on the periphery of the ligand exposed to solvent environment allows further engineering of the surface polarity between that of the polar and nonpolar analogs. Further, the Au@24 material exhibits hysteresis, where the polarity of the surface is dependent on previous solvent exposure, which allows for this material to be a model system for controlled surface wetting. NPs with these surface binding ligands form highly crystalline superlattice films where NP separations are tailored from 2.5 nm (for Au@22) to 5.6 nm (for Au@23) as the dendron generation is increased. We foresee the future utility of such ligands in controlling and guiding the assemblies of NPs into functional architectures and at various interfaces, such as liquid-liquid interfaces, emulsions, and membranes. In addition, we envision the widespread utility of dendritic ligands with polar end-groups in biomedical applications as they introduce water solubility and

are monodisperse in nature that rules out any ligand size related discrepancies when conducting *in vitro* or *in vivo* experiments.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental details, full characterization of organic compounds, additional microscopy, and supporting spectroscopy can be found in the Supporting Information.

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Notes

The authors declare the following competing financial interest: Aspects of this work have been included in a U.S. provisional patent filing.

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