

Plasmonic Chiroptical Response of Silver Nanoparticles Interacting with Chiral Supramolecular Assemblies

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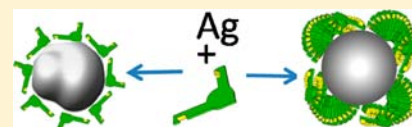
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S Supporting Information

ABSTRACT: Silver nanoparticles were prepared in aqueous solutions of chiral supramolecular structures made of chiral molecular building blocks. While these chiral molecules display negligible circular dichroism (CD) as isolated molecules, their stacking produced a significant CD response at room temperature, which could be eliminated by heating to 80 °C due to disordering of the stacks. The chiral stack-plasmon coupling has induced CD at the surface plasmon resonance absorption band of the silver nanoparticles. Switching between two plasmonic CD induction mechanisms was observed: (1) Small Ag nanoparticles coated with large molecular stacks, where the induced plasmonic CD decayed together with the UV molecular CD bands on heating the solution, indicating some type of electromagnetic or dipole coupling mechanism. (2) Larger Ag nanoparticles coated with about a monolayer of molecules exhibited induced plasmonic CD that was temperature-independent. In this case it is estimated that the low chiroptical response of a molecular monolayer is incapable of inducing such a large chiroptical effect, and a model calculation shows that the plasmonic CD response may be the result of a slight chiral shape distortion of the silver nanoparticles.



1. INTRODUCTION

Circular dichroism is a powerful tool for studying the conformation of chiral molecular structures.^{1–3} Whereas in biology chiral superstructures are encountered everywhere, such man-made objects are more difficult to synthesize. Self-assembly is a powerful tool to create unique chiral molecular superstructures.⁴ It was shown that by cooperative hydrogen bonding⁵ and combination of π - π stacking^{6–8} chiral supramolecular structures may be formed in aqueous environments. Until recently, a great challenge was to create these structures in protic media due to the difficulty of using hydrogen bonding to direct chiral columnar assemblies. A recent success⁹ opened the way to couple chiral supramolecular structures with plasmonic nanoparticles (NPs), which are usually easier to prepare as aqueous colloids. Coupling between chiral molecules and noble metal NPs can lead to interesting phenomena such as absorbance and circular dichroism (CD) enhancement,¹⁰ CD induction at the plasmon excitation of noble metal NPs by the molecular chirality,¹¹ and even creation of chiral NPs.¹² So far, plasmonic CD induction has been observed in only a few systems.^{13–15} The most studied system consisted of clusters of tens of gold atoms with strongly binding chiral thiol-containing molecules, where both surface distortion and electronic interaction effects were used to explain the induced metal states CD.^{16–18} It was also shown both experimentally¹⁹ and theoretically²⁰ for small metal clusters that chiral atomic

configurations can be created and even separated to their two enantiomers.²¹

Other reported cases of CD induction in larger metal nanoparticles with weakly bound chiral molecules are currently described by simple models that require additional experimental support.²² One of the simpler mechanisms suggested for CD induction is a purely electronic dipole–dipole interaction. However, such an effect is expected to be fairly weak and would probably require either very large chiral molecules with strong chirality and strong dipolar coupling¹⁵ or a cumulative interaction of the metal core with a large number of chiral molecules oriented in the same way.¹⁹ The second option may be realized in a system of strongly chiral, uniformly oriented supramolecular stacks. Along with the plasmonic chirality induced by attached biomolecules, purely excitonic and plasmonic CDs can be created in properly designed nanostructures.^{23,24}

In this work we use the power of temperature-dependent CD spectroscopy to analyze chiral molecule–silver nanoparticle assemblies. Increasing the relative metal:molecule concentration ratio led to an increase in the average particle size and reduction in molecular stack size. This was accompanied by an apparent change in the induced plasmonic CD from a

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temperature-dependent effect to a temperature-independent effect. Model calculations and the experimental findings for the larger particles with a monolayer molecular coating indicate that structurally chiral PNPs may have been created.

2. EXPERIMENTAL SECTION

The water used was ultrapure (18 M Ω -cm), obtained from a USF ELGA UHQ system. Silver nitrate (>99.0%) and sodium borohydride (>99.0%) were purchased from Sigma-Aldrich. The chiral molecular ligand (CM) and a similar achiral analogue (ACM), as drawn in Figure 1(A), were synthesized according to ref 25.

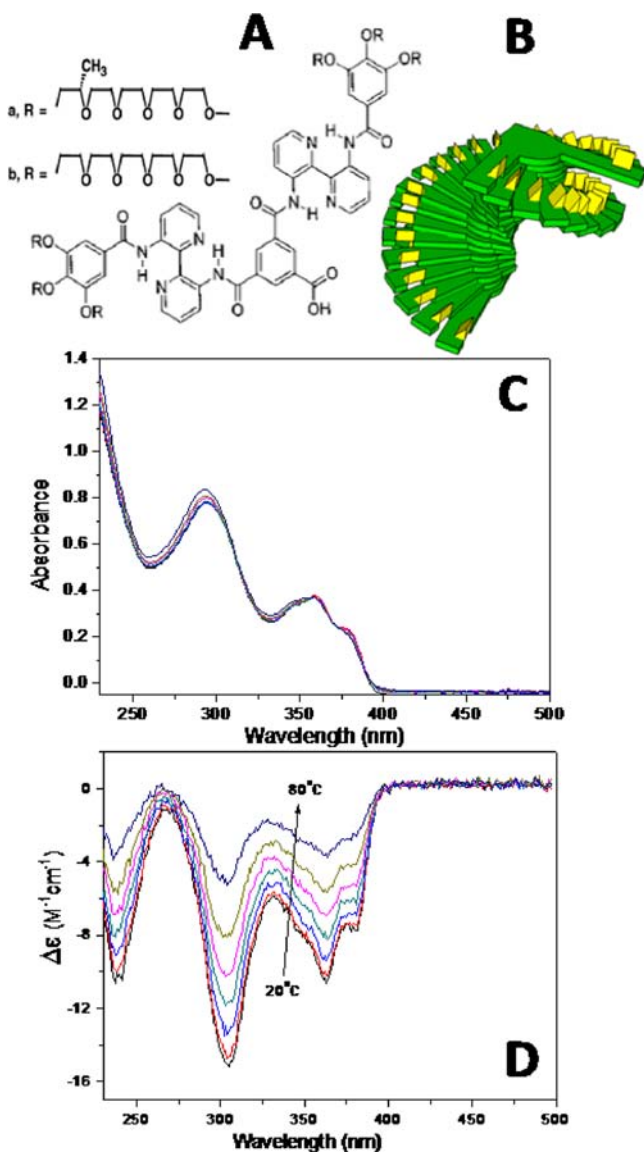


Figure 1. (A) Molecular structure of CM a and achiral molecule b. (B) Illustration of the self-assembly of the CM. (C) Absorbance spectra of a. (D) CD spectra of the pure CM solution (a) as a function of solution temperature.

2.1. Silver Nanoparticle Synthesis. Stock solutions of 10 mM AgNO $_3$, ACM, and CM were prepared in water, separately. We used fresh solutions of 10 mM sodium borohydride in each synthesis. For NP synthesis with Ag:CM 1:1; 16 μ L of Ag $^+$ 10 mM, 16 μ L of CM 10 mM, and 4 mL of water were added to a round-bottom flask with magnetic stirrer, and after 5 min of stirring 16 μ L of 10 mM sodium borohydride was added. The other ratios of Ag:CM were prepared in

the same method, except for changing the volume of silver nitrate solution that was added; the CM concentration was constant for all the samples. The exact same processes were repeated with ACM for part of the samples.

2.2. Characterization. Absorption measurements were performed on a Varian Carry-5000 spectrophotometer. CD measurements were performed on an Applied Photophysics Chirascan CD spectrometer. The samples of Ag:CM 8:1–32:1 were diluted before measurement to keep the absorbance values below 0.9, and then the CD and absorbance were multiplied by the dilution factor. The unit conversion from mdeg to $\Delta\epsilon$ was done according to estimation of the silver NP concentration, while for the bare molecule it was by the molecule concentration.

Temperature dependence measurements: after heating the sample to the desired temperature, the sample was equilibrated for \sim 15 min before measuring; the measurement was repeated after an additional 5 min to make sure that the samples reached equilibrium.

All samples were deposited on carbon-coated copper grids (SPI) for transmission electron microscopy (TEM) analysis. Images were recorded using a Philips FEI Tecnai F20 FEG-TEM.

2.3. Calculations. All calculations were done according to the model described in refs 17 and 26. An outline of the basic principles and details of the parameters appear in the Supporting Information.

3. RESULTS AND DISCUSSION

We used aqueous solutions of molecular stacks of CM and the analogous ACM with C $_1$ symmetry (Figure 1A). Similar chiral molecules of C $_3$ symmetry were previously studied by Meijer and co-workers and found to form chiral supramolecular stacks that exhibited large CD signals.^{9,26} An artist view of a possible chiral assembly of the CM molecules is depicted in Figure 1B. Dynamic light scattering measurements showed that for a 0.04 mM solution of the CM molecules aggregates with a hydrodynamic radius of \sim 150 \pm 20 nm were formed, which, assuming a 1–2 nm thickness for each molecule, indicates molecular aggregate size of the order of hundred molecules. The CM molecules were mixed with silver ions at various concentration ratios, and to this mixture was added an excess of sodium borohydride as a strong reducing agent. This led to the formation of silver nanoparticles with CM coating, as seen in the transmission electron microscope (TEM) images of the Ag:CM samples of 4:1 and 32:1 (see Figure 2a,b). The average Ag nanoparticle size depended on the Ag:CM ratio; for example, a 4:1 ratio yielded an average size of 3.8 \pm 1.4 nm and a 32:1 ratio yielded 6.3 \pm 2.8 nm particles (Supporting Information, Figure S1). While in the Ag-CM nanoparticle case no reliable light scattering hydrodynamic radius data could be obtained, these measurements consistently showed that the radii were reduced to well below 100 nm, indicating high affinity of the CM to the silver surface.

As mentioned above, CD spectroscopy is an excellent method to look at molecular and supramolecular configurational changes.²⁷ In many cases absorbance changes are indicators of π - π stacking.²⁸ In the present case, changes in the CD intensity as a function of temperature, while the absorbance remained constant, imply that the π - π stacking does not play a significant role in the CM's molecular aggregates and that CD is induced by interaction of the aromatic moieties with other parts of the neighbor molecules. The aggregation in water is probably due to hydrophobic interactions of their aromatic cores. Apparently, the arene–arene interactions of the aromatic cores create a hydrophobic microenvironment that allows for structuring via the specific, solvent-sensitive interactions.^{9,22}

The CM has several functional chemical groups, such as poly(ethylene glycol) (PEG) providing solubility in water and

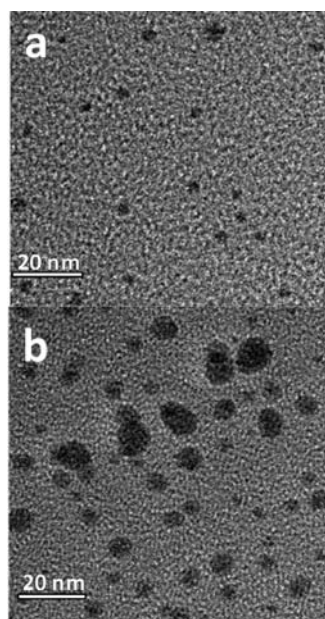


Figure 2. (a) TEM micrograph of the NPs prepared from Ag:CM 4:1 ratio. (b) TEM micrograph of the NPs prepared from Ag:CM 32:1 ratio.

carboxylic acid and nitrogen-containing aromatic rings that provide high affinity toward the silver surface. Its lowest absorption band is close to the plasmon resonance of silver (absorption threshold at ~ 400 nm). All of this makes it ideal to

use for capping silver nanoparticles in an aqueous dispersion. It should be further emphasized that the CD signal of isolated CM molecules, at wavelengths above 220 nm (as in the case of the C_3 analogue) is negligible, as the influence of the chiral modification on the PEG groups barely interacts with the electronic states of the aromatic moieties in the core of the molecules.⁹

The CD and absorbance spectra of Ag-CM NPs prepared with CM are shown in Figure 3b–d (and Supporting Information, Figure S2). We can identify 4 Cotton effect peaks in the CD spectra related to 4 molecular absorption features (238, 309, 363, and 380 nm, see Figure 3) and one new peak corresponding to the surface plasmon resonance of the NPs (~ 400 – 430 nm). This new CD peak is the result of interaction between the chiral environment and the electrons of the metal particles. In Figure 3 it can be seen that the 238 and 309 nm molecular CD peaks did not change on forming the CM coated Ag NPs, while the 363 and 380 nm peaks were changing both in the CD signal (from negative to positive) and in absorption, indicating a stronger interaction of the molecular and metal states.

When relatively low Ag:CM ratios are used, the temperature dependence of the molecular CD lines is as strong as in the case of pure CM dissolved in water. On increasing the silver to CM ratio (while keeping the CM at the same concentration for all samples), the spectral properties of the system change. In Figure 3d it can be seen that for large (~ 6.5 nm) Ag:CM ratios (32:1) there is almost no temperature dependence at the CD lines. Another important change that occurs in the CD spectra with high Ag:CM ratio is the shape and relative magnitude of

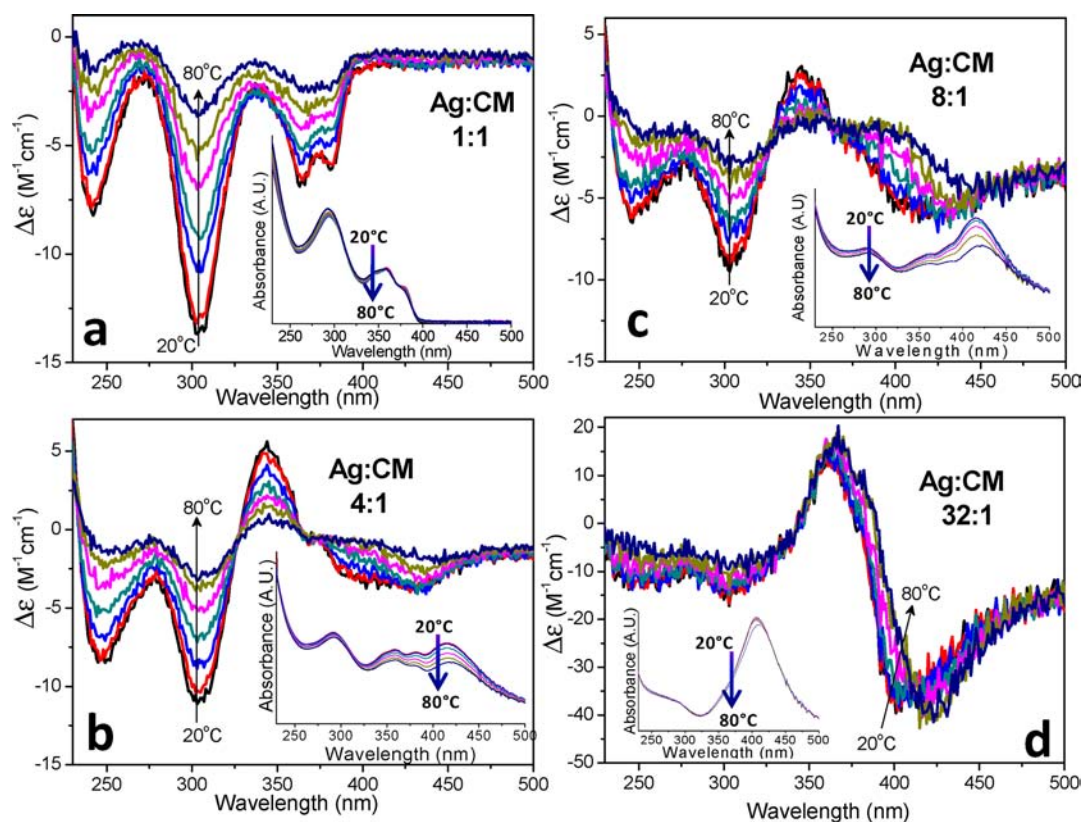


Figure 3. CD spectra of silver particles coated with CM prepared from different Ag:CM ratios, measured as a function of temperature: (a) 1:1, (b) 4:1, (c) 8:1, (d) 32:1. The insets show the respective absorbance spectra series, which typically undergo only a small change with temperature. The concentration used for calculation of $\Delta\epsilon$ is the estimated nanoparticle concentration.

the plasmonic CD. On going from Ag:CM ratio of 8:1 to 32:1 the plasmonic CD feature at ~ 410 nm becomes much stronger than the molecular CD, by more than the expected $\times 4$ factor, and its shape changes from primarily negative to strongly bisignate.

A rough estimate of the amount of CM molecules that cover a $\sim 6\text{--}7$ nm silver particle, based on an assumption of an effective molecular footprint area of ~ 100 \AA^2 on the silver surface, is shown in Table 1. As will be shown below, the

Table 1. Calculation of the Amount of Molecules per Ag Particle (or Stack, in the Absence of Ag) for the Various Preparations

Ag:CM molar ratio	estimated no. of CM molecules per particle	estimated no. of molecules per stack
0:1		~ 100
1:1	3828	49
2:1	1914	25
4:1	957	12
8:1	478	6
16:1	239	3
32:1	120	1.5

affinity of the CM to the silver NP surface is higher than the molecule–molecule interaction; hence it appears that with the growth of the Ag NPs the CM molecules will densely coat the NPs, breaking the CM stacks as much as needed for fully coating the growing NPs. In the case of the 32:1, it is estimated that the Ag particles are covered by roughly a monolayer of CM molecules. As mentioned above, the chiroptical effect of a single CM molecule is negligible, and thus a long-range CD induction mechanism such as multipolar or electromagnetic type would not be expected to yield a significant induced plasmonic CD signal. The insensitivity of the CD spectra of this sample to temperature also indicates in the direction of no or very small molecular stacks attached to the nanoparticles, which also strengthens the above-mentioned assumption that the binding of the CM to the silver surface is stronger than the CM stacking. On the other hand, for the 4:1 sample, it is estimated that there are ~ 10 molecules per stack, on average, coating the nanoparticles. Nevertheless, it seems that the increase in the thermal energy is not sufficient to dissociate the aggregates, though it may affect the CD by disordering the molecules in the aggregates.

Consequently, these results may indicate the different mechanisms that dominate the CD induction effect in the two extremes of metal:molecule ratios. The bisignate plasmonic CD line of the 32:1 sample (Figure 3d) can be reproduced by a model calculation of the plasmonic CD response of a spherical silver particle of 3.5 nm diameter with a helical groove of 0.75 nm depth as shown in Figure 4. More details on this calculation appear elsewhere²⁹ and in the Supporting Information. It can be seen that the model was able to quantitatively reproduce both the absorption and CD spectra with slight wavelength shifts due to the difference in particle size between the model and the experimental average. If this is indeed the case, the 32:1 sample would probably be the largest chiral colloidal particles reported so far. It should be noted that although the average size of the as-prepared particles in the 32:1 sample is 6.3 nm, smaller size dispersions (~ 3.0 nm) obtained by precipitation of the larger particle in a centrifuge produced similar temperature-insensitive CD (see Supporting Information, Figure S3).

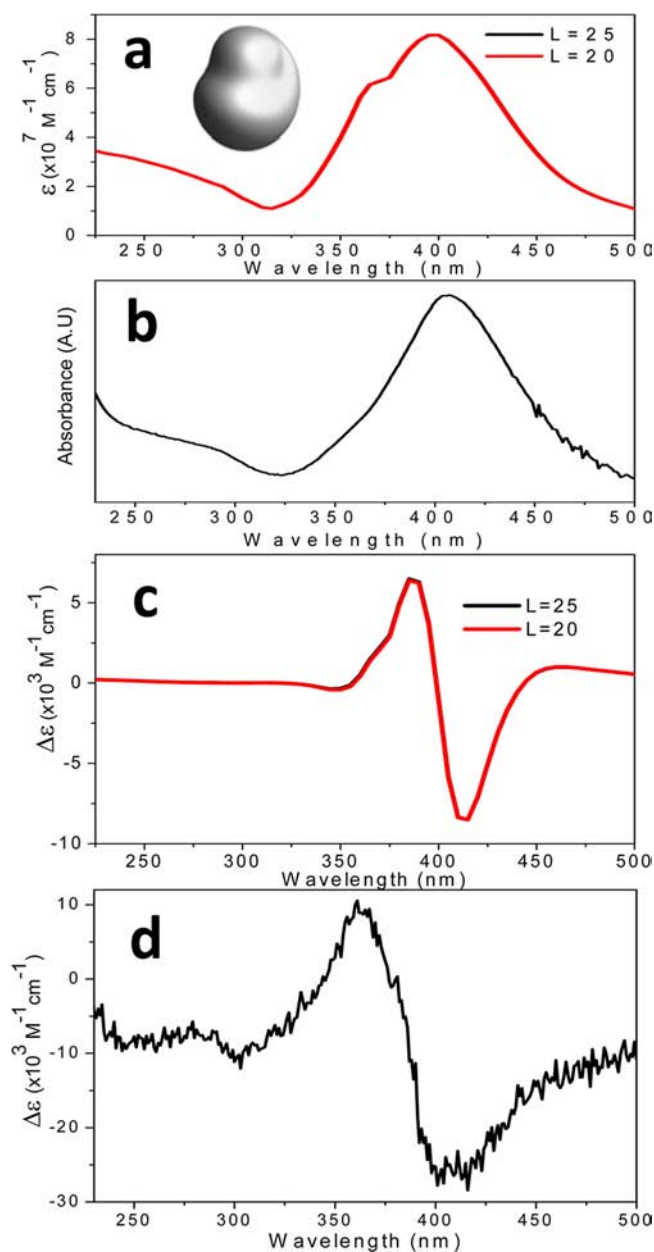


Figure 4. (a) Calculated absorbance spectrum of a chiral silver twister particle (shown as an inset) and (b) the measured one (ratio 32:1). (c) Calculation of the CD spectrum of the twister particle and (d) the measured one (ratio 32:1). Each calculated graph has two different curves which correspond to $L = 20$ and $L = 25$ spherical harmonics used in the calculation, showing that the calculation has converged.

For smaller Ag:CM ratios, the plasmonic CD line is almost monopolar, smaller in amplitude than the molecular CD, and strongly temperature-dependent. This indicates that this CD induction is largely caused by a dipolar mechanism. The induced plasmonic CD at the small NPs with low Ag:CM ratio was modeled using a dipolar interaction mechanism. The calculation was done for different molecule–particle separations and compared to the experimental results. Figure 5a shows the result of the dipolar model calculation, where for separations that are ≥ 3 nm the induced plasmonic CD is weaker than the CD of the molecular UV absorption lines, as in the experimental case. This rough model is brought only to show that electromagnetically induced CD is possible for this

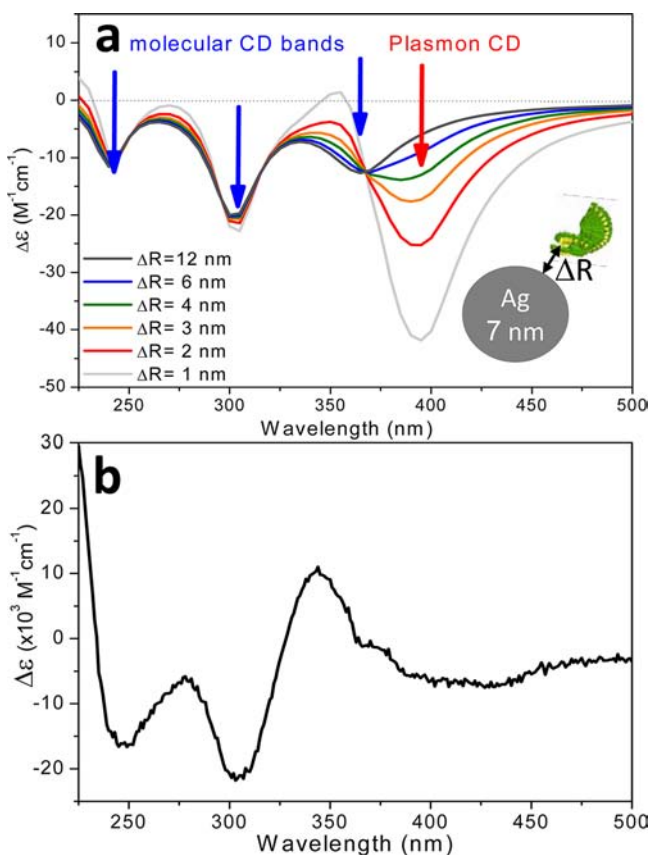


Figure 5. (a) Calculated CD spectra of Ag particles coated with CM for various separation distances of the CM from the particle surface. The blue arrows mark the molecular absorption lines, and the red one marks the plasmon resonance. The model used a 7 nm silver particle. (b) The experimental CD spectrum of Ag:CM 4:1 (Figure 3b).

system. It is possible that a mixture of the two mechanisms (chiral shape and dipolar interaction) acts in this case, as there is a small positive CD signal around 350 nm in the experimental data that is not described by this simple model. The temperature-independent red tail in the induced plasmonic CD peak in the experiment seen around 450 nm at the 8:1 sample (also at 4:1, to a smaller extent) might be due to a small population of structurally chiral, nonspherical shapes of the Ag nanoparticles that already exist at this relatively small Ag:CM ratio.

To verify the claims on the above-mentioned mechanisms the following experiment was done. After the NP solution of 32:1 was prepared, additional CM ($\times 12$ of the original concentration) was added, and the CD spectra before and after the extra CM addition were compared as seen in Figure 6a. After the CM was added to the 32:1 solution, the bisignate CD profile in plasmon resonance region did not change. Upon heating, as seen earlier, the plasmonic CD peak did not change with temperature, while the molecular peaks corresponding to the new molecular stacks were diminished with temperature. It is interesting to note that the molecular UV CD lines before the addition of the extra CM are negligible in amplitude relative to those appearing after the addition of the extra CM, again corroborating the assumption that no stacks are originally formed at the surface of the NPs in the 32:1 sample.

A similar experiment was repeated for the Ag:CM 4:1 sample with similar results, also shown in Figure 6b. The weak plasmonic CD does not change upon the addition of CM (in

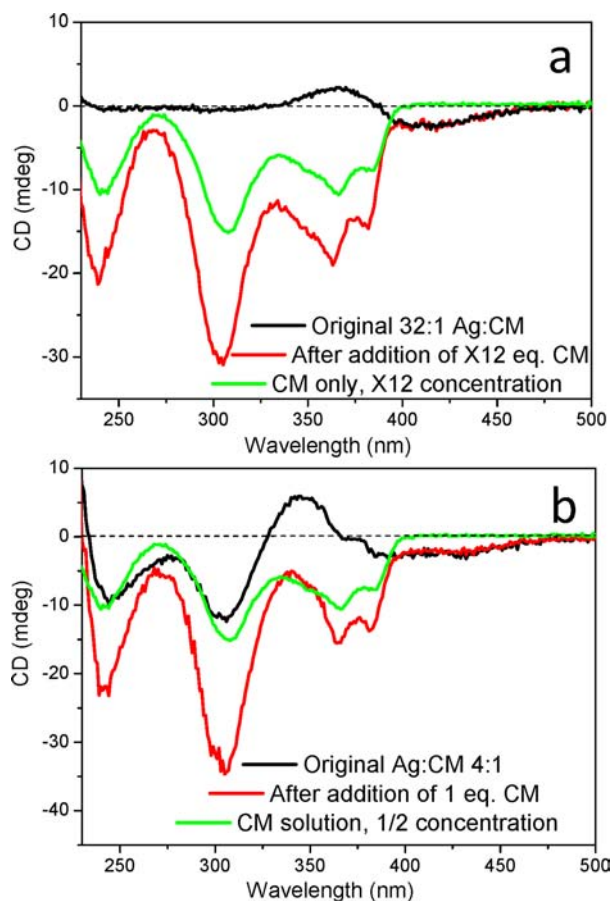


Figure 6. (a) Ag:CM 32:1 sample before and after the addition of $\times 12$ CM equiv, relative to the original CM concentration. Compared to the same ($\times 12$) pure CM solution. Note the almost complete absence of CM molecular CD lines in the as prepared 32:1 sample. (b) Ag:CM 4:1 sample before and after addition of 1 equiv of CM and again, compared to pure CM solution (diluted by a factor of 2 relative to the NP sample).

this case it was increased by only $\times 2$). This finding conforms, in principle, to our mechanistic picture. The average stack in this sample was estimated to have ~ 12 molecules (Table 1), which would surely be larger than 1 nm, and hence additional molecules bound to such stacks would typically be at distances > 1 nm from the NP surface. For NPs of several nm in size the plasmon decay distance would typically be ≤ 1 nm from the NP surface. Consequently, the additional molecules would not interact with the NPs surface plasmon resonance modes.

In order to learn the significance of the molecular configuration dependence, the NPs were prepared with the achiral molecules (ACM) instead of the CM (Figure 1a) at a 4:1 Ag:ACM ratio. As expected there was no induced plasmonic CD signal (see Figure 7b). In order to further test the conclusion about the dipolar induction mechanism for the 4:1 sample, the CM coated NPs were mixed with $\times 40$ excess of ACM. As shown in Figure 7a, this caused the induced plasmonic CD to significantly decay. This effect shows that indeed, in the 4:1 sample, the CD induction mechanism is primarily dipolar in origin with perhaps only a small fraction of the sample behaving as intrinsically chiral.

Figure 7b display the opposite experiment, of NPs prepared with ACM and then mixed with excess CM. Here an induced plasmonic CD is not created. Note that Figure 7a,b is focused

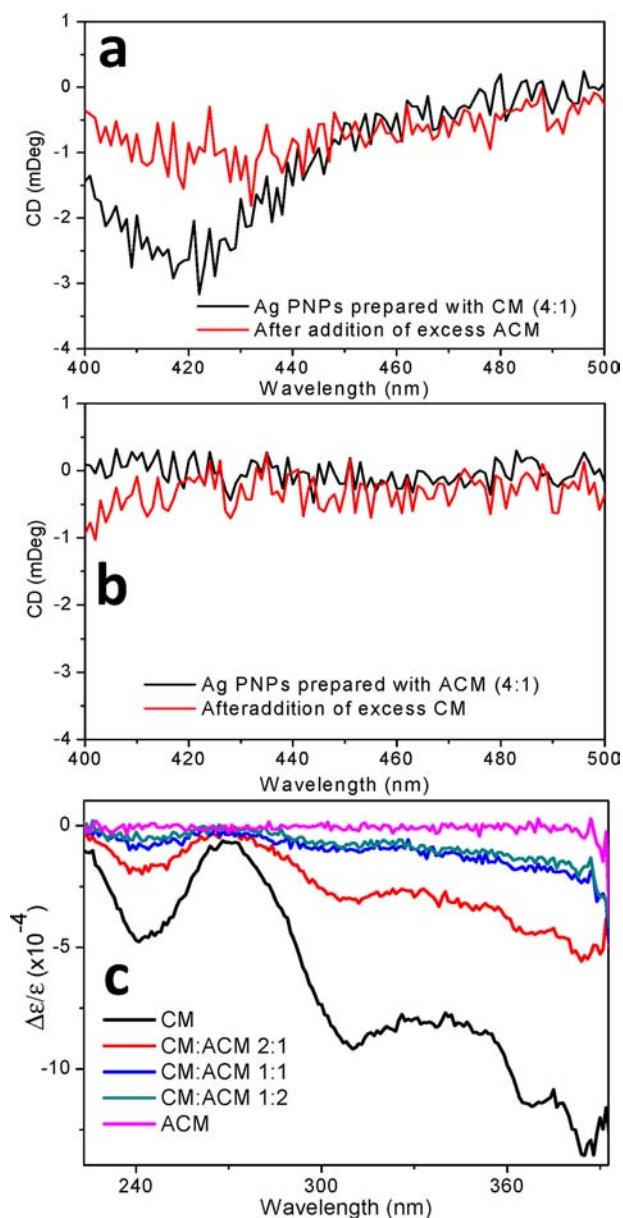


Figure 7. (a) CD spectra around the plasmon peak wavelength. First, Ag particles were prepared in the presence of CM (4:1), and then 40 times higher concentration of ACM was added and a second CD measurement was performed 72 h later. (b) Ag NPs were prepared with ACM (4:1), CD was measured, and then CM was added at a 40 times higher concentration relative to the original ACM concentration and CD spectrum was measured again 72 h later. (c) Dissymmetry factor for various molecular mixtures with different ratios of CM:ACM without silver.

only on the plasmonic CD signal at wavelengths >400 nm. This indicates that in order to achieve the plasmonic CD induction, the NPs need to be formed in the presence of the chiral molecules. There may be two reasons for such a requirement: (1) The molecules that serve as surface anchors adsorb strongly and are difficult to exchange by the free molecules of the other species. (2) The configuration of the CM around the NPs is crucial for the induced CD, and if the ACM is gradually exchanged for CM, this special oriented coating cannot be achieved. In the other case, where ACM is added to NPs formed with CM, it is enough to exchange part of the CM for

ACM to disrupt the special chiral stacking and null the induced CD, as in the increased temperature case.

An interesting question is whether the CM is able to amplify chirality as in the C_3 analogue case, and alternatively, which fraction in the stacks should be substituted by ACM in order to significantly reduce the chiral structure of the stacks.^{9,22} Figure 7c shows the dissymmetry factor ($\Delta\epsilon/\epsilon$) spectra at the molecular lines (wavelength <400 nm) of various CM:ACM mixtures without silver. It can be seen that the dissymmetry signal is reduced by more than 50% upon the addition of 30% of ACM, and with 50% ACM it goes down by an almost 1 order of magnitude. This indicates a high sensitivity of the CM stack conformations to the interference of the ACM, a much higher sensitivity compared to that of the C_3 analogue.²²

Despite the simplicity of the models used here they are well supported by the experimental data obtained under different preparation conditions, namely, an induced plasmonic CD as related to dipolar (or multipolar) interactions and a plasmonic CD due to intrinsically (structurally) chiral particles. Moreover, according to the two simple theoretical models, the plasmonic CD is expected to be not highly sensitive to the size of the nanoparticles. Characterization of the system reveals that the configuration of the CM around the NPs is a very important factor in the achievement of the dipolar CD induction effect. High resolution TEM micrographs show a large overall shape and size variety. This makes it difficult to point at possible relevant shape distortions as opposed to random shape fluctuations and to identify consistent shapes such as chiral grooves, in particular due to their expected sub nm dimensions.

4. CONCLUSION

In summary, the interaction between metal NPs and chiral supramolecular assemblies was investigated. These supramolecular structures give rise to CD induction at the nanoparticle's surface plasmon resonance when adsorbed to silver NPs. The study revealed that two cases can be distinguished: (1) A large Ag:CM ratio probably creates Ag NPs with slight structural chirality ("twisters"). These NPs may be the largest size intrinsically chiral metal nanoparticles reported so far (~ 6 nm). They exhibit temperature-independent plasmonic CD that is significantly more intense than the CD response of the CM. (2) A small Ag:CM ratio probably creates stacks of >10 molecules, with a conformation that is temperature-dependent and an induced CD at the wavelength region of the plasmon resonance that is weaker than the CD of the molecule. In this second case a dipolar interaction model provides a plausible mechanism for the induced CD. In both cases the experimental results corroborate with the models that were presented. The use of chiral supramolecular assemblies may further be extended toward new molecular template systems and formation of metal nanostructures with outstanding chiroptical properties, due either to larger intrinsic chirality of the NPs or to stronger chiroptical induction on the NPs surface plasmon resonance.

■ ASSOCIATED CONTENT

Supporting Information

Particle size statistics, additional CD and absorbance spectra, and theoretical model description. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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