VIP Nanostructures

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Molecular Structure–Function Relations of the Optical Properties and Dimensions of Gold Nanoparticle Assemblies**

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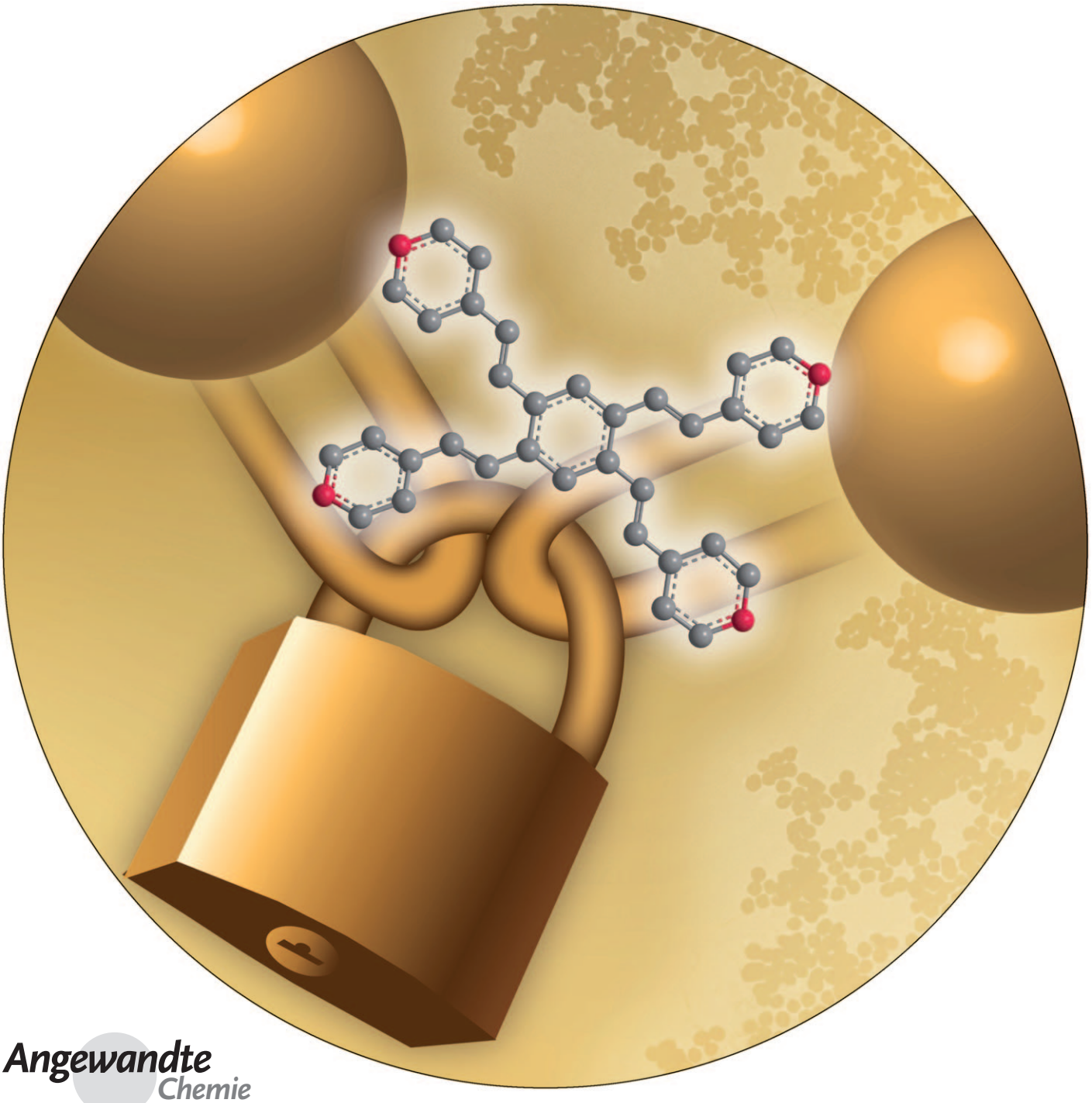
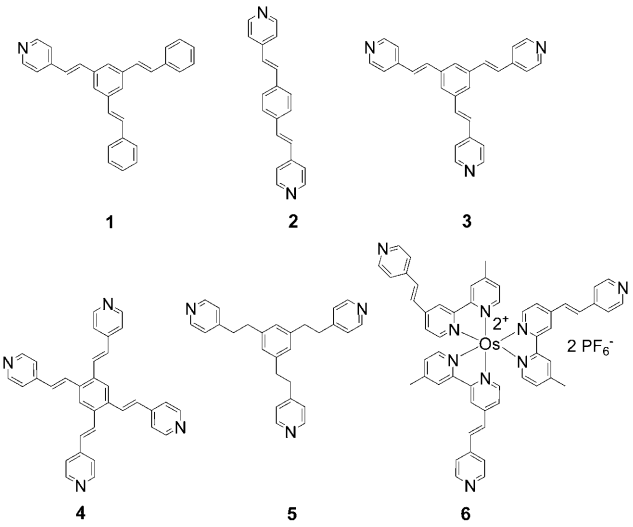


Structurally well-defined organic compounds have the ability to direct the formation of large assemblies in solution and in the solid state.[1] Control over nanoparticle (NP) assemblies has been reported with a variety of cross-linkers (CLs), including polymers, charged molecules, dendrimers, and biomolecules (e.g., DNA, antigen–antibody, and avidin–biotin) to name but a few.[2–4] In particular, the formation of NP assemblies has been studied as a function of the size or charge characteristics of the CL.[4] Nevertheless, designing and predicting the properties and structure of hybrid NP-based assemblies based on a given molecular structure is still a difficult task. Systematic variation of the CL (2D vs. 3D geometry, number of potential NP binding sites, size, symmetry, etc.) is needed to gain fundamental insight into the factors that control the physicochemical properties of the resulting hybrid assemblies.

Herein, we demonstrate that the molecular structure of the organic CL, in addition to the number of available coordination sites, has a significant impact on the formation and optical properties of AuNP assemblies. A series of CLs with one to four pyridyl moieties (**1**–**6**, Scheme 1)[5,6] were reacted with solutions of citrate-capped AuNPs with a homogeneous size distribution of (11.8 ± 1.3) nm (Figure S1 in the Supporting Information). In particular, solutions of the CLs in THF were added stepwise to aqueous solutions of freshly prepared AuNPs. A distinct color change from red to deep blue was observed with CLs **3**–**6**, thus indicating that the AuNPs readily formed assemblies (Figure 1, insets).[7] In contrast, the red color of the AuNP solution remained unchanged in the monopyridyl system (**1**, Figure 1) and with pyridine. The color change for CL **2** was relatively small. Our observations demonstrate that the color of the AuNP-based assemblies can be controlled as a function of the structure and concentration of the organic component (Figure 1).

The UV/Vis spectra of the assemblies formed with compounds **2**–**6** show changes upon increasing the CL concentration from 0.0 to 1.8 μM. Specifically, the intensity of the coupled surface plasmon band at $\lambda_{max} = 600$–635 nm increases, while the plasmon band at $\lambda_{max} = 519$ nm decreases. In addition, a red shift of approximately 10 nm is observed for the plasmon bands of compounds **3**–**6** (Figure 1). The change in the latter plasmon band indicates the formation of AuNP-based assemblies, while the former reflects changes in the contacting dielectric media (i.e., citrate ions versus the CLs) on the AuNPs surfaces.[8] The optical spectra of the AuNP



Scheme 1. Molecular structures of the cross-linkers (CL)[5,6] used to direct the AuNP–CL assembly formation and properties.

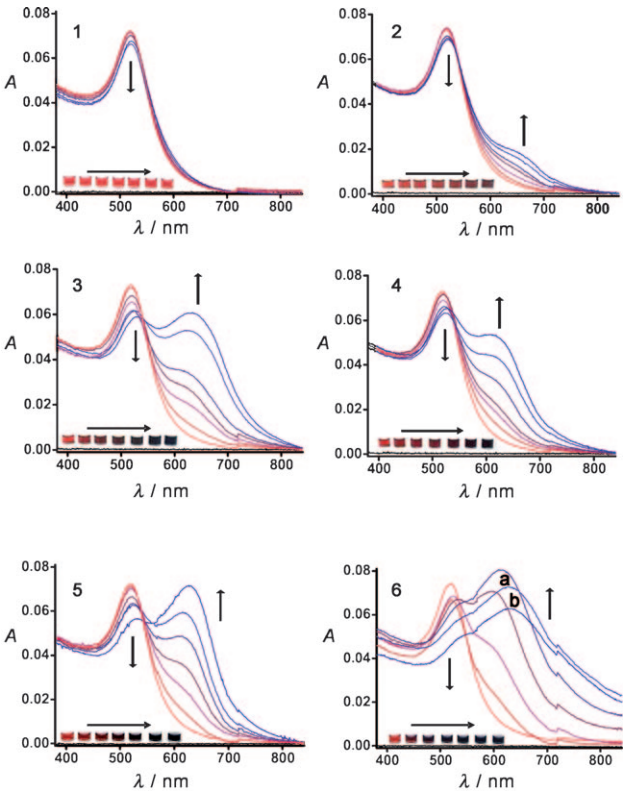


Figure 1. UV/Vis spectra of the hybrid AuNP–CL-based assemblies. The labels correspond to the molecular structures shown in Scheme 1. Solutions of the CL (**1**–**6**; 50 μM) in THF were added (0–36 μL in 6 μL increments) to 1 mL aqueous solutions of AuNPs to give a final concentration of 1.8 μM. Spectra were recorded immediately after mixing the components. High concentrations of CL **6** (1.5–1.8 μM) resulted in a decrease in absorbance arising from precipitation of the assemblies (traces a and b). Insets: photographs of the solutions at each incremental addition of CL.

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solutions mixed with compounds **1** or pyridine show only minor changes. A small shift of approximately 2 nm and dampening of the plasmon bands implies that the stabilizing capping layer of the AuNPs was exchanged with these ligands. However, no coupled plasmon band is observed, thus indicating that the AuNPs mainly exist as independent entities for these two compounds. Interestingly, the intensity and broadening of the coupled surface plasmon band suggest that formation of the AuNP assemblies is related to the number of pyridyl moieties (between one and four), where the degree of assembly formation increases in the order: pyridine $\approx$ **1** $\ll$ **2** $<$ **4** $<$ **3** (Figure 2). Other structural factors also play a dominant role in the AuNP assembly formation. For instance, the saturated analogue of **3** (compound **5**) results in a significantly higher degree of NP assembly formation, which is similar to that obtained with the charged CL **6**.

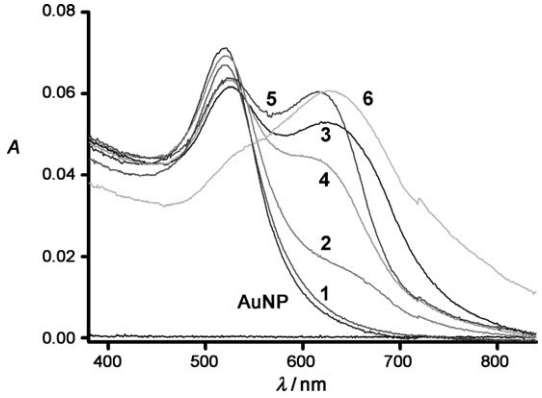

Figure 2. Comparison of the UV/Vis spectra of the hybrid AuNP–CL-based assemblies in aqueous solutions with a concentration of compounds **1**–**6** of 1.5 μM. Spectra were recorded immediately after mixing the components.

Compound **6** differs from the other cross-linkers in that it has a +2 charge. It is known that the use of charged species as cross-linkers results in NP assemblies formed by Coulombic interactions.[9] When CL **6** was added to the AuNP solutions, extensive assemblies were formed. Similar results were obtained with $[Os(bpy)_3]^{2+}$ (bpy = 4,4′-bipyridyl) complexes that bear zero or one pendant pyridyl arms (Scheme S1 in the Supporting Information), thus indicating that NP–pyridyl coordination is, in this case, not a requirement for NP assembly formation. Thus, in these charged systems, the level of control that the CL structure has over the formation and optical properties of the NP assembly seems minimal.

The TEM images (Figure 3 and Figure S3 in the Supporting Information) show increasing AuNP aggregation as a function of the number of pyridyl units and/or the molecular geometry, which is in good agreement with the UV/Vis analysis (see above). Solvent-free conditions were used for these measurements and, therefore, only the qualitative structures of the AuNP assemblies in solution are reflected in these images. Systems formed with CL **1** or pyridine showed isolated spheres and small aggregates on the grid, whereas the other systems (**2**–**6**) form larger assemblies of

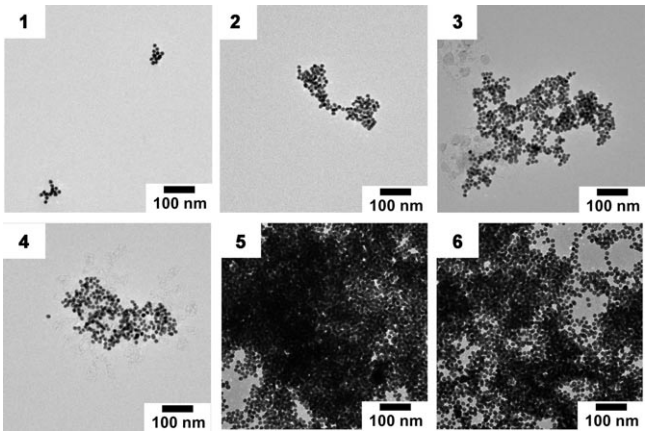

Figure 3. Representative TEM images of the AuNP–CL assemblies. The labels correspond to the molecular structures shown in Scheme 1 and the UV/Vis spectra given in Figure 1. Additional TEM images are provided in Figure S3 in the Supporting Information.

varying dimensions. This result clearly shows that a higher number of pyridyl units is a requirement for aggregation of the AuNPs. TEM analyses indicate that the level of aggregation for CLs **2**–**4**, which have a structure with between two and four binding sites, is somewhat similar (Figure 3), although each of these systems has unique optical properties (Figure 1). Significantly larger and denser assemblies are observed for CLs **5** and **6**.

To provide some insight into the origins of the experimental findings, density functional theory (DFT) calculations (at the M06/SDB-pc1//M06L/SDB-pc1/DFBS level of theory, see the Supporting Information for details) were carried out. The organic CLs **1**–**5** and pyridine were coordinated to one to four Au_8 clusters, and the binding energies (BEs) were determined (Table 1). From these DFT results, it would seem that electronic effects are minor and the BEs for CLs **2**–**5** are very similar. It is interesting to note that the BEs decrease for each additional gold cluster coordinated to the CL. Coordination of the fourth gold cluster to CL **4** is slightly unfavorable. The small size of the gold cluster, which is essential to make the calculations feasible, precludes steric interactions in the AuNP–CL structures but, nonetheless, should reproduce trends in the electronic nature of the Au–CL binding. If one were to consider the geometric limitations of this system, it is clear that none of CLs considered are large enough for them to bind to more than two NPs simultaneously. (A full analysis is provided in the Supporting

Table 1: DFT binding energies (BE) of 1–4 Au_8 clusters bound to CLs **1**–**5**.[a]

CL	BE per Au_8	BE(1)[b]	BE(2)[b]	BE(3)[b]	BE(4)[b]
1	−22.4	−22.4			
2	−21.6	−22.0	−21.1		
3	−20.5	−21.1	−20.7	−19.7	
4	−20.2	−21.2	−20.9	−19.7	1.0
5	−20.9	−21.8	−21.0	−19.9	

[a] Binding energies reported in kcal mol^{-1}. [b] Binding energy of the first, second, third, and fourth cluster to the CL.

Information.) However, the CLs are capable of linking two AuNPs. The saturated nature of CL **5** allows for greater flexibility, which, in turn, allows the system to better link between two AuNPs. This flexibility allows the CL to keep the AuNPs at a larger angle, thereby reducing any possible repulsive interactions.

Our observations indicate that for CLs **2**–**5**, weak intermolecular interactions, such as π–π interactions or dipole–dipole interactions, do not play a significant role, but rather AuNP assembly formation results from coordination by the pyridyl groups. The molecular geometries of a series of pyridyl-based CLs are expressed in the formation and optical properties of these AuNP assemblies. The structural differences of the CLs at the molecular level have been expressed in the formation of the AuNP assemblies at the submicrometer level. Apparently, electronic factors do not seem to play a major role in influencing assembly formation. The use of a more flexible (saturated) CL (e.g., **5** as compared to CLs **2**–**4**), however, results in a higher degree of aggregation. These systems follow the observations by Lehn regarding the gentle balance between rigidity and flexibility.[10] This seems to be better realized in the saturated system, resulting in more extensive assembly formation. Furthermore, charged CLs (e.g., **6** and its derivatives) do not allow for fine control over the degree of nanoparticle aggregation that can be achieved by the use of neutral, organic CLs (e.g., **2**–**5**).

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