Heterosupramolecular Chemistry: Programmed Pseudorotaxane Assembly at the Surface of a Nanocrystal**

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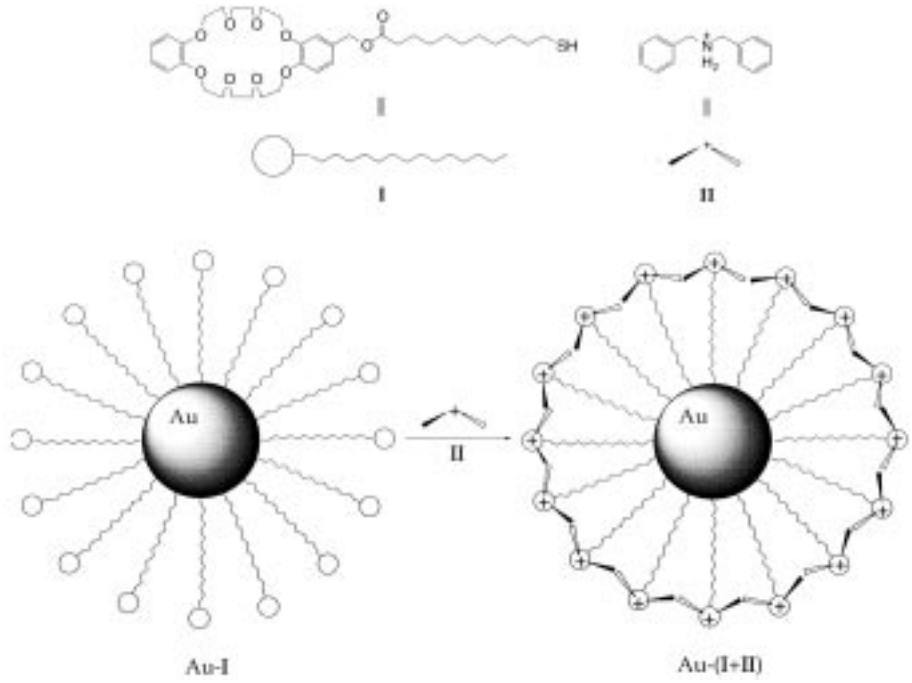
The size-dependence of the electronic and optical properties of metal and semiconductor nanocrystals has been studied in detail.[1] These investigations have been facilitated by the preparation of dispersions of essentially defect-free nanocrystals that possess narrow size distributions and are stabilized by chemisorbed long-chain alkanes.[2–8] Fundamental insights into the evolution of bulk electronic and optical properties in metals and semiconductors have resulted.[3, 9]

Increasingly, it is the collective electronic and optical properties of metal and semiconductor nanocrystals that are being investigated.[3, 10, 11] These studies are being facilitated by the preparation of organized nanocrystal assemblies.[1, 5, 10–14] Of particular interest is how the size-dependence of the electronic and optical properties of the constituent nanocrystals may be exploited to tune their collective properties.

Organized nanocrystal assemblies are generally prepared at an air–water interface using Langmuir-Blodgett techniques (two-dimensional),[12] or on a suitable substrate by controlled solvent evaporation (three-dimensional).[10] Both approaches, however, are limited by the fact that only relatively simple nanocrystal architectures may be realized. For this reason, strategies that may permit the assembly of complex nanocrystal architectures are of particular interest.

One strategy is to prepare a dispersion of nanocrystals that is stabilized by molecules that incorporate one or more binding sites. These binding sites serve to define uniquely the position of a nanocrystal from a dispersion in the nanocrystal architecture being assembled. Upon mixing a number of such dispersions each nanocrystal recognizes and binds selectively a nanocrystal from another dispersion or a well-defined region on the surface of a suitably patterned substrate. By this means it should be possible to program the parallel assembly of identical, multiple copies of the desired nanocrystal architecture in solution or at a substrate. Underpinning the above strategy are efforts directed toward the development of a systematic chemistry of both condensed phase and molecular components, that is, a systematic heterosupramolecular chemistry.[15–17]

Despite a growing number of examples of programmed nanocrystal assembly in solution, much remains to be done.[15–21] Specifically, there is a pressing need for a robust model system, the study of which could provide detailed insights into the factors that control nanocrystal assembly in solution or at a suitable substrate. Toward this end, we have prepared a dispersion of gold nanocrystals that possess a narrow size distribution and are stabilized by a chemisorbed monolayer of **I**. It was expected that these nanocrystals, denoted Au-**I**, would recognize and bind selectively the dibenzylammonium cation **II** in solution to form the pseudorotaxane-containing assembly Au-(**I** + **II**).[22–24] Presented here are the findings of our initial studies that show these expectations are largely justified and, interestingly, which point to similarities between the binding of a molecule in solution by the receptor sites on the surface of a nanocrystal and the binding of a drug molecule by the receptor sites on the surface of a cell.[25]



Transmission electron microscopy (TEM) establishes that the average diameter of a gold nanocrystal in Au-**I** is 42 ± 8 Å (Figure 1).[26] Elemental analysis establishes that the average number of **I** adsorbed at the surface of each nanocrystal is

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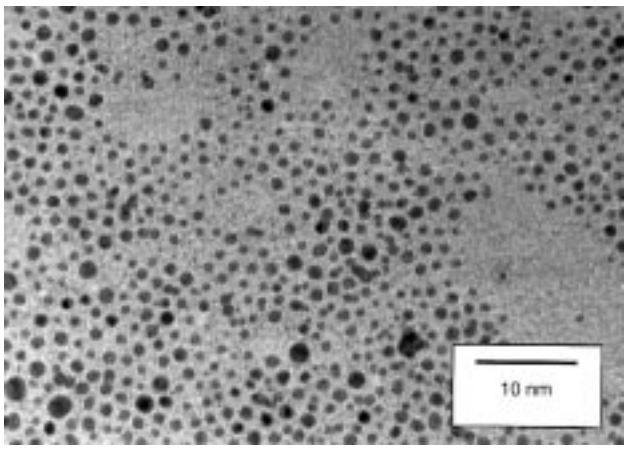

Figure 1. TEM picture of gold nanocrystals stabilized by a chemisorbed monolayer of **I** (Au-**I**).

300.[27] On this basis[28] it has been calculated that the average surface area occupied by each molecule **I** is 18 Å^2. This value is smaller than that for a monolayer of **I** self-assembled at a planar gold substrate (21 Å^2),[29] but, as expected, somewhat larger than those reported for an alkanethiol adsorbed at the surface of a gold nanocrystal (16 Å^2).[30] These findings can be explained by the extreme curvature of the gold nanocrystal and the steric hindrance associated with the terminal crown moiety of **I**, respectively.

The ^{1}H NMR spectra of **I** and Au-**I** in $CDCl_3$ are shown in Figure 2. In solution the resonances assigned to the methylene protons α, β, and γ to the sulfur atom in **I** arise at δ 2.52 (2H, q), 1.61 (2H, m), and 1.36 (2H, m), respectively. When, however, **I** is adsorbed at the surface of a gold nanocrystal, these same resonances are broadened to such an extent that the α-methylene proton resonance is no longer observed.[30] This observation contrasts with the fact that the resonances assigned to the methylene protons α, β, and γ to the ester moiety in **I** are not significantly broadened. Thus, it is concluded that all molecules of **I** in Au-**I** are adsorbed at the surface of a gold nanocrystal. It is also concluded, because of the curvature of the gold nanocrystal, that the motions of the methylene groups close to the sulfur atoms and the surface of the gold nanocrystal are constrained. However, this situation does not pertain to the methylene groups near the oxycarbonyl group in that region of **I** that extends into the solvent.

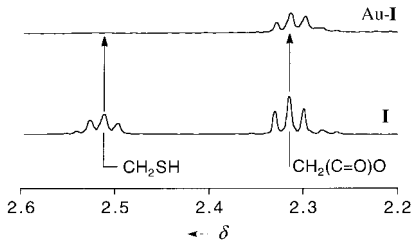

Figure 2. Section of the ^{1}H NMR spectrum of free **I** and Au-**I**.

Dibenzo[24]crown-8, the precursor of **I**, recognizes and binds **II** selectively in $CDCl_3$.[22–24] It has also been established that the crown is threaded by **II** to form a [2]pseudorotaxane. It was expected, therefore, that **I** would also recognize and bind **II** selectively in $CDCl_3$ and that a similar complex would be formed. The ^{1}H NMR spectra (not shown) of **I**, **II**, and an equimolar mixture of **I** and **II**—(**I** + **II**)—were measured in $CDCl_3$ to establish whether or not this is the case. The observed changes in the spectra are similar to those reported for an equimolar mixture of dibenzo[24]crown-8 and **II**.[22–24] Furthermore, an analysis of these changes also yields values for K_a (2.7×10^4 L mol^{-1}) and ΔG^0 (-25 kJ mol^{-1}) that are similar.[24] On this basis, it is concluded that an equimolar mixture of **I** and **II** self-assemble to form a [2]pseudorotaxane.[22–24] Having established that an equimolar mixture of **I** and **II** forms a [2]pseudorotaxane, it was expected that Au-**I** would recognize and bind **II** selectively to form a similar complex under similar conditions. To establish whether or not this is the case, the ^{1}H NMR spectra of Au-**I**, **II**, and an equimolar mixture of Au-**I** and **II**—Au-(**I** + **II**)—were measured in $CDCl_3$ (Figure 3).

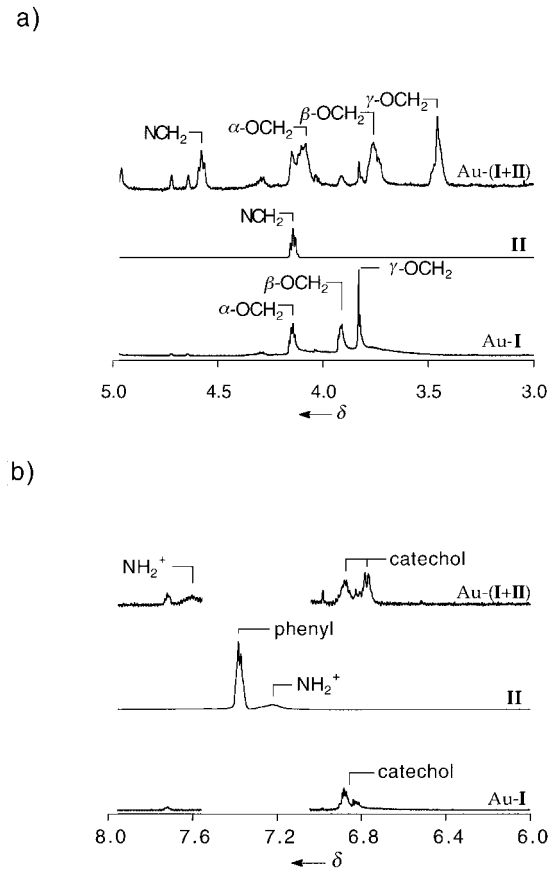

Figure 3. Two sections of the ^{1}H NMR spectra of Au-**I**, **II**, and an equimolar mixture of Au-**I** and **II**.

In the aliphatic region of the spectrum of Au-**I** (Figure 3a), the resonances assigned to the α-, β-, and γ-OCH_2 protons of the dibenzo[24]crown-8 ring moiety appear at $\delta = 4.14$ (8H, t), 3.92 (8H, t), and 3.83 (8H, s), respectively. In the aliphatic region of the spectrum of **II** the resonance assigned to the benzylic methylene protons of the dibenzylammonium cation appear at $\delta = 4.15$ (4H, t). In Au-(**I** + **II**), the resonances assigned to the α-, β-, and γ-OCH_2 protons of the diben-

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zo[24]crown-8 moiety are shifted upfield by $\Delta\delta = 0.05$, 0.15, and 0.37, respectively, while the resonance assigned to the benzylic methylene protons of the dibenzylammonium cation are shifted downfield by $\Delta\delta = 0.43$. In the aromatic region (Figure 3b), the resonance assigned to the catechol protons of the dibenzo[24]crown-8 moiety of Au-**I** appear at $\delta = 6.80 - 6.92$ (7H, m), while the resonances assigned to the phenyl and ammonium cation protons of **II** appear at $\delta = 7.37 - 7.40$ (10H, m) and 7.22 (2H, brs), respectively. The resonance assigned to the catechol protons of Au-**I** in Au-(**I** + **II**) are shifted upfield by $\Delta\delta = 0.1$, while the resonances assigned to the phenyl and ammonium cation protons of **II** are shifted upfield and downfield by $\Delta\delta = 0.2$ and 0.4, respectively. The above spectral changes are similar to those previously reported for an equimolar mixture of dibenzo[24]crown-8 and **II**,[22–24] and observed for an equimolar mixture of **I** and **II**. On this basis it can be concluded that an equimolar mixture of **I**, adsorbed at the surface of a gold nanocrystal, and **II** form a [2]pseudorotaxane.

A quantitative analysis of the spectra in Figure 3 indicates that 86% of the dibenzo[24]crown-8 binding sites at the surface of each gold nanocrystal in Au-**I** are complexed with a dibenzylammonium cation **II**. As a consequence Au-(**I** + **II**) precipitates from $CDCl_3$ over a period of three hours. It should be noted, that addition of 10% by volume of CD_3CN results in the precipitated nanocrystals being re-dispersed. It should also be noted, however, that the fraction of complexed dibenzo[24]crown-8 binding sites at the surface of each gold nanocrystal in Au-**I** is reduced to 45%. As the crown ether binding sites incorporated in **I** are not in solution but are adsorbed at the surface of a gold nanocrystal, a single point determination of K_a based on the nominal concentrations of Au-**I**, **II**, and Au-(**I** + **II**) is not appropriate.[25] The preparation of a Scatchard plot with a slope equal to $-K_a$ and an intercept equal to NK_a [Eq. (1)] is more appropriate.[25, 31]

$$\frac{P}{C} = NK_a - PK_a \qquad (1)$$

P is the fraction of crown binding sites complexed with a cation, C is the concentration of **I** added to solution, and N is the number of crown binding sites on each gold nanocrystal. The Scatchard Plot obtained, however, is highly nonlinear (Figure 4a). The positive slope observed at low concentration C indicates that the fraction of crown receptor sites that have bound a dibenzylammonium cation is less than expected. This, in turn, indicates that binding is co-operative. Under such conditions an analysis based on the preparation of a Hill Plot (Figure 4b) with a slope equal to the Hill coefficient n_H, and an intercept equal to $-n_H \lg(1/K_a)$ [Eq. (2)] is necessary.[25, 32] The slope of the Hill Plot in Figure 4b yields a value for n_H equal to 2.21 (correlation coefficient $R = 0.991$), which is consistent with the nonlinearity of the Scatchard Plot, and confirms a positive co-operation in the binding process exists.

$$\lg\left(\frac{P}{1-P}\right) = n_H \lg C - n_H \lg\left(\frac{1}{K_a}\right) \qquad (2)$$

The origin of the positive co-operativity is likely to result from the following: An increased affinity of **II** for the surface of Au-**I** as the surface of the nanocrystal become progressively more polar/hydrophilic. It should be noted that the above suggestion is consistent with the observation that Au-(**I** + **II**) precipitated from $CDCl_3$. Our results raise the intriguing possibility of using such systems as models for cell–drug binding studies and, possibly, as in vivo sensors for such interactions.

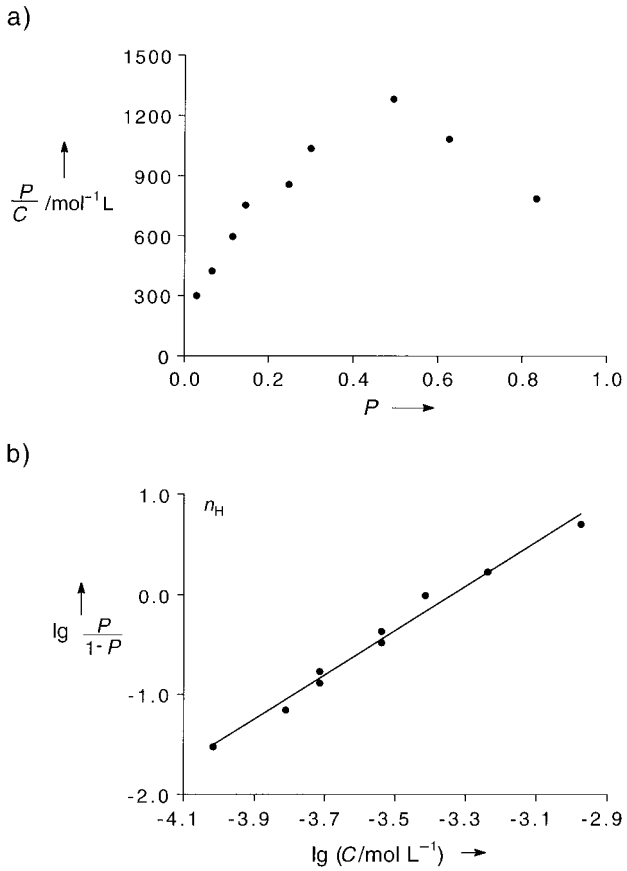

Figure 4. a) Scatchard Plot and b) Hill Plot for Au-**I** (0.25–1.00 equivalents of **II** added).

Experimental Section

(2-Formyl)dibenzo[24]crown-8, prepared as described in detail elsewhere,[33] was converted into (2-hydroxymethyl)dibenzo[24]crown-8,[34] which was subsequently coupled to 11-sulfanylundecanoic acid to form **I**.[35] Compound **II** was prepared as described elsewhere.[22]

Gold nanocrystals, stabilized by chemisorbed **I**, were prepared following the method reported by Brust et al.:[36] $HAuCl_4$ (0.155 g) in deionized H_2O (15 mL) was added to a phase transfer catalyst $n Oct_4NBr$ (1.101 g) in $CDCl_3$ (12 mL), and the resulting mixture stirred vigorously for approximately 10 min. The organic layer was recovered, the stabilizer (**I**, 0.070 g) in $CDCl_3$ (4 mL) and the reducing agent ($NaBH_4$, 0.190 g) in H_2O (13 mL) added, and the resulting mixture stirred overnight at room temperature. Gold nanocrystals were precipitated by concentrating the reaction mixture (to 4 mL), adding it EtOH (300 mL), and stirring vigorously. The precipitated nanocrystals were isolated by centrifugation, re-dissolved in a minimum of $CDCl_3$, and re-precipitated by addition of EtOH (30 mL). Gold nanocrystals stabilized by chemisorbed **I**, Au-**I**, were recovered by centrifugation and dried in air.

^1H NMR studies were carried out on Au-**I** and employed 1×10^{-6} M (particle concentration) dispersions in $CDCl_3$, corresponding to a 4×10^{-4} M solution of adsorbed **I**. Studies on equimolar mixtures of Au-**I** and **II** employed 1.0 mL of the above dispersion to which had been added a 30 μL aliquot of 1.35×10^{-2} M stock solution of **II** in CD_3CN, which

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corresponded to a final concentration of the added compound of 4×10^{-4} M. Binding studies on Au-**I** employed a 3×10^{-6} M (particle concentration) dispersion in $CDCl_3$ and CD_3CN (10 vol%), corresponding to a 1×10^{-3} M solution of adsorbed **I**. The desired volume of a 1.35×10^{-2} M stock solution of **II**, which corresponds to between 0.25 and 1.00 equivalents, was added to 0.7 mL of the above dispersion.

All ^{1}H NMR spectra were recorded at 25 °C using a Varian 500 FT spectrometer. Transmission electron micrographs were recorded using a JEOL 2000 FX Temscan (150 K eV) for samples deposited on carbon coated copper grids.

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[26] The reported values for Au-**I** are based on a statistical analysis of the diameter of two hundred nanocrystal cores of each as determined by TEM (Figure 1).
[27] Elemental analysis established that the percentage of organic material (by weight) in Au-**I** is 31.1 % (C 19.80, H 2.34, N 0.00). The percentage C by weight was extrapolated to infer the ratio of organic material to metal.
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