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Heterosupramolecular Chemistry: Recognition Initiated and Inhibited Silver Nanocrystal Aggregation by Pseudorotaxane Assembly

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Abstract: Near size-monodisperse silver nanocrystals stabilized by chemisorption of a mixture of an alkane thiol (85%) and an alkane thiol incorporating a dibenzo-24-crown-8 moiety (15%) have been prepared. Using dynamic light scattering and nuclear magnetic resonance, it is shown that addition of bis-dibenzylammonium dication initiates aggregation of the silver nanocrystal dispersion by pseudorotaxane assembly. It is also shown that addition of excess dibenzylammonium cation or dibenzo-24-crown-8 inhibits further aggregation. This novel demonstration of controlled nanocrystal aggregation points the way toward the programmed assembly of complex nanocrystal architectures in solution.

Introduction

Size-monodisperse nanocrystals of a wide range of materials have been prepared and their size-dependent electronic and magnetic properties studied.[1−9] However, it is the collective electronic and magnetic properties of organized assemblies of size-monodisperse nanocrystals that are increasingly the subjects of investigation.[1,3,5,10−14] Interest in these organized assemblies is enhanced by the fact that it ought to be possible to fine-tune their properties by controlling the size of constituent nanocrystals. The findings of these and related investigations suggest that it may be possible to self-assemble complex nanocrystal architectures in solution or on a substrate.

Generally, organized assemblies of nanocrystals are prepared at an air−water interface (two-dimensional),[12] or on a suitable substrate by controlled solvent evaporation (three-dimensional).[10] However, both approaches are limited by the fact that only relatively simple nanocrystal architectures can be realized. For this reason, strategies that permit the assembly of complex nanocrystal architectures are of particular interest.

One strategy is to prepare a dispersion of nanocrystals stabilized by molecules incorporating one or more binding sites. These binding sites should serve to define uniquely the position of a nanocrystal in the architecture to be assembled. Upon mixing a number of such dispersions, each nanocrystal should recognize and bind 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 on a substrate.

We have recently reported[22] the preparation and characterization of a dispersion of gold nanocrystals possessing a narrow size distribution and stabilized by a chemisorbed monolayer of a dodecane thiol derivative covalently linked to dibenzo[24]-crown-8. These nanocrystals were shown to recognize, and bind

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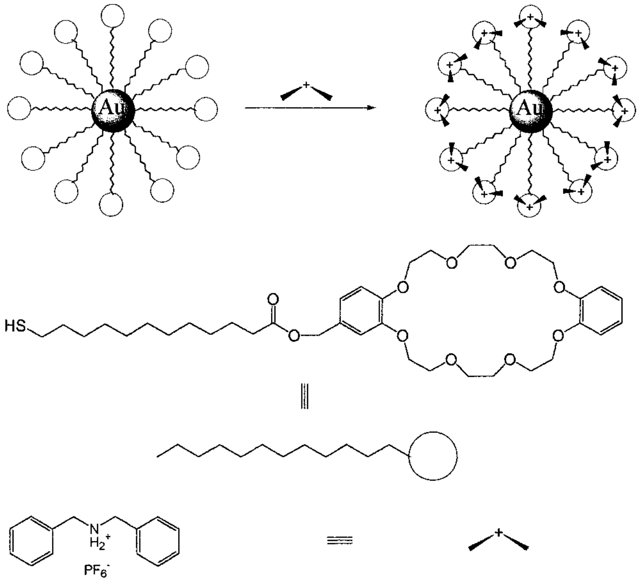
Scheme 1. A Gold Nanocrystal, Stabilized by a Monolayer of an Alkane Thiol Incorporating a Dibenzo-24-crown-8 Moiety, Binds a Dibenzylammonium Cation To Form a [2]Pseudorotaxane at Its Surface



in solution, a dibenzylammonium cation,[22-25] forming the [2]-pseudorotaxane-coated nanocrystal shown in Scheme 1.

Here, we report the preparation and characterization of near size-monodisperse silver nanocrystals, stabilized by chemisorption of a mixture of an alkane thiol (85%) and an alkane thiol covalently linked to a dibenzo-24-crown-8 moiety (15%). It is established that addition of a bis-dibenzylammonium dication initiates aggregation of the silver nanocrystal dispersion (Scheme 2). It is also established that subsequent addition of an excess of the dibenzylammonium cation or dibenzo-24-crown-8 compound inhibits aggregation.

Experimental Section

Preparation of Compounds. The compounds used in the present study are shown in Scheme 3. **1** and **5** were used as supplied by Aldrich. Compounds **2**, **3**, and **4** were prepared as described in detail elsewhere.[22-25] All compounds were characterized by elemental analysis and by ^{1}H NMR spectroscopy.

Calculated for **1** ($C_{12}H_{26}S$): C, 71.21; H, 12.95; S, 15.89. Found: C, 71.19; H, 13.12; S, 15.55. ^{1}H NMR δ ($CDCl_3$): 0.88 (t, 3H, J = 7.0 Hz), 1.22 (m, 16H), 1.36 (m, 2H), 1.61 (m, 2H), 2.52 (q, 2H, J = 7.0, 3.5 Hz).

Calculated for **2** ($C_{36}H_{54}O_{10}S$): C, 64.25; H, 7.96. Found: C, 63.8; H, 7.86. ^{1}H NMR δ ($CDCl_3$): 1.27 (m, 12H), 1.39 (m, 2H), 1.61 (m, 2H), 2.32 (t, 2H, J = 7.0 Hz), 2.52 (q, 2H, J = 7.0, 3.5 Hz), 3.82−3.85 (m, 8H), 3.89−3.97 (m, 8H), 4.12−4.24 (m, 8H), 5.04 (s, 2H), 6.85−6.95 (m, 7H).

Calculated for **3** ($C_{22}H_{26}N_2P_2F_{12}$): C, 43.42; H, 2.63; N, 4.61. Found: C, 43.16; H, 2.84; N, 4.51. ^{1}H NMR δ (CD_3CN): 4.24 (s, 4H), 4.25 (s, 4H), 7.14−7.25 (br m, 4H), 7.45−7.51 (m, 14H).

Calculated for **4** ($C_{14}H_{16}NPF_6$): C, 48.98; H, 4.66; N, 4.08. Found: C, 47.71; H, 4.34; N, 4.63. ^{1}H NMR δ (CD_3CN): 4.20 (s, 4H), 7.39−7.53 (m, 10H), 9.19 (br s, 2H).

Calculated for **5** ($C_{24}H_{32}O_8$): C, 64.28; H, 7.14. Found: C: 64.19; H, 7.24. ^{1}H NMR δ ($CDCl_3$): 3.84 (m, 8H), 3.92 (m, 8H), 4.14 (m, 8H), 6.86−6.90 (m, 8H).

Preparation and Modification of Nanocrystals. Silver nanocrystals stabilized by **1**, denoted Ag-**1**, were prepared following the two-phase synthesis developed by Brust et al. and size-selective precipitation was used to isolate near size-monodisperse Ag-**1** nanocrystals.[26] These nanocrystals were characterized by transmission electron microscopy (TEM) and elemental analysis.[27] TEMs were obtained using a JEOL 2000 FX TEMscan (at an acceleration voltage of 80 kV) for samples deposited on carbon-coated copper grids. The preparation of samples for TEM involved deposition of a few drops of a dispersion of the nanocrystals in $CHCl_3$ onto a carbon-coated TEM grid.

Ag-**1** was modified by chemisorbing a compound incorporating the appropriate receptor site, namely **2**, at the surface of the Ag nanocrystal. Specifically, **1** adsorbed at the surface of Ag-**1** was exchanged with **2** from solution, using similar methods to those described by Murray and co-workers.[28] Briefly, a dispersion in $CHCl_3$ (5 mL) of Ag-**1** (1.34×10^{-6} mol dm^{-3} nanocrystals, 1.76×10^{-3} mol dm^{-3} **1**) was stirred in the presence of **2** (8.84×10^{-4} mol dm^{-3}) for 48 h under an Ar atmosphere. The modified silver nanocrystals Ag-**2**, on which both **1** and **2** are chemisorbed, were recovered by centrifugation (Sorvall Instruments, USA; A500 rotor, 5000 rpm, 5 min), following addition of EtOH (50 mL). The above nanocrystals were characterized by TEM and elemental analysis.[29]

Aggregation of Modified Nanocrystals. ^{1}H NMR spectroscopy was used to study the interactions at a molecular level between Ag-**2** and **3** in solution. Specifically, an ^{1}H NMR spectrum was obtained upon mixing a dispersion of Ag-**2** (5.7×10^{-6} mol dm^{-3} nanocrystals, 8.6×10^{-4} mol dm^{-3} **2**) in $CDCl_3$ (0.80 mL) and a solution of **3** (1.7×10^{-3} mol dm^{-3}) in CD_3CN (0.20 mL). These relative concentrations correspond to a 2:1 ratio of **2** to **3**. A ^{1}H NMR spectrum was also measured upon mixing a solution of **2** (7.79×10^{-3} mol dm^{-3}) in $CDCl_3$ (0.80 mL) and a solution of **3** (1.56×10^{-2} mol dm^{-3}) in CD_3CN (0.20 mL). All ^{1}H NMR spectra were recorded using a Varian 500 FT spectrometer. Dispersions and solutions used in ^{1}H NMR spectroscopic studies were prepared from dry samples of the desired nanocrystal or compound by addition of $CDCl_3$ or CD_3CN.

Dynamic light scattering (DLS) was used to study the aggregation of Ag-**2** initiated by addition of **3**. Specifically, DLS was used to monitor the increase in the hydrodynamic radius of the scattering entity upon mixing a dispersion of Ag-**2** (3.25×10^{-8} mol dm^{-3} nanocrystals, 4.95×10^{-6} mol dm^{-3} **2**) in $CHCl_3$ (1.00 mL) and a solution of **3** (4.95×10^{-4} mol dm^{-3}) in MeCN (0.005 mL). These relative concentrations correspond to a 2:1 ratio of **2** to **3**. DLS was also used to monitor aggregation upon mixing a dispersion of Ag-**1** (3.25×10^{-8} mol dm^{-3} nanocrystals) in $CHCl_3$ (1.00 mL) and a solution of **3** (4.95×10^{-4} mol dm^{-3}) in MeCN (0.005 mL); upon mixing a dispersion of Ag-**2** (3.25×10^{-8} mol dm^{-3} nanocrystals, 4.95×10^{-6} mol dm^{-3} **2**) in $CHCl_3$ (1.00 mL) and a solution of **4** (9.9×10^{-4} mol dm^{-3}) in MeCN (0.005 mL); and upon mixing a dispersion of Ag-**2** (3.25×10^{-8} mol dm^{-3} nanocrystals, 4.95×10^{-6} mol dm^{-3} **2**) in $CHCl_3$ (1.00 mL) and an aliquot of MeCN (0.005 mL).

DLS was also used to study the aggregation of Ag-**2** initiated by addition of **3**, prior to and following the addition of excess **4** and **5**.

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(27) Found for Ag-**1**: C, 12.91; H, 2.08; S, 2.74. ^{1}H NMR δ ($CDCl_3$): 0.77−0.91 (br, 3H), 1.22−1.35 (br m, 16H), 1.35−1.42 (br, 2H). (Other resonances not observed.)

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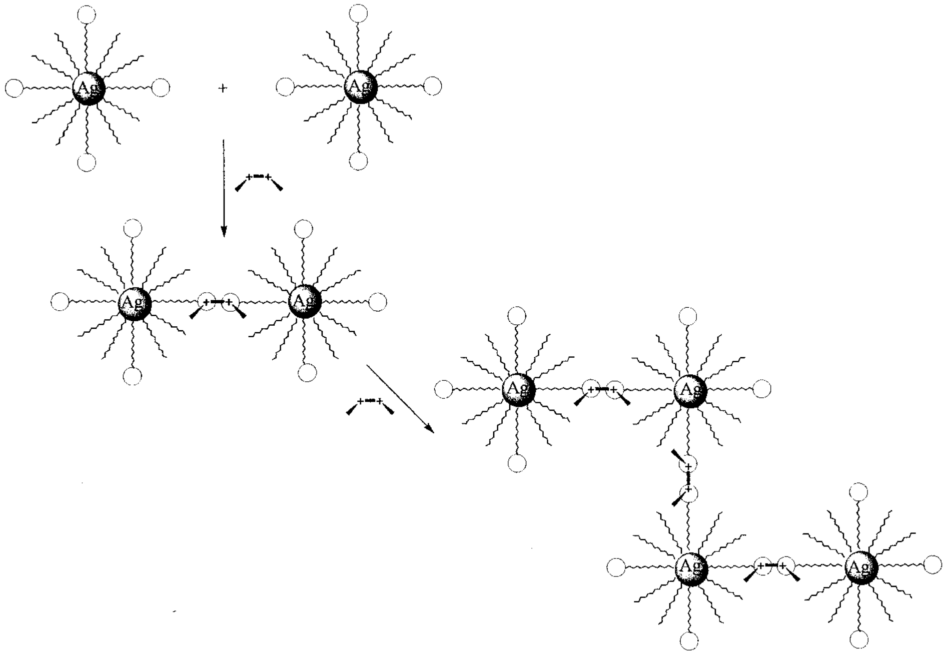
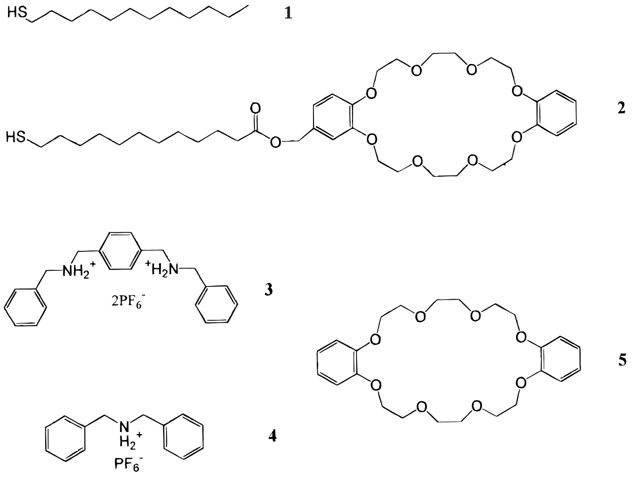
(29) Found for Ag-**2**: C, 19.84; H, 3.72; S, 4.84. ^{1}H NMR δ ($CDCl_3$): 0.74−92 (br, 3H), 1.12−1.48 (br s, 16H), 2.24−2.41 (br, 2H), 3.82−3.85 (br, 8H), 3.89−3.97 (br, 8H), 4.12−4.24 (br, 8H), 5.00−5.04 (br, 2H), 6.83−6.93 (br, 7H). (Other resonances not observed.)

Scheme 2. Two Silver Nanocrystals, Stabilized by a Monolayer of Alkane Thiol[a]



[a] Some of the alkane chains incorporate a dibenzo-24-crown-8 moiety. These nanocrystals recognize and bind a bis-dibenzylammonium dication to form a [3]pseudorotaxane, thereby linking the two nanocrystals.

Scheme 3. The Compounds Used in the Present Study



Aggregation of Ag-**2** was described above. The effect of subsequent addition of **4** (2.48×10^{-3} mol dm^{-3}) and **5** (4.95×10^{-2} mol dm^{-3}) in MeCN (0.001 mL) was monitored for 24 h. The above additions yielded a 2:1 ratio of **2** to **4** and a 1:10 ratio of **2** to **5**.

DLS studies were performed using a Malvern PCS-4700 instrument, equipped with a 256-channel correlator. The 488.0 nm line of a Coherent Innova-70 Ar ion laser was used as the light source (100 mW). The temperature was maintained at 25.00 ± 0.02 °C throughout by an external circulator. All dispersions and solutions used were filtered through an Anotop syringe filter (0.02 μm) and all additions made using a 10 μL microsyringe (Hamilton, USA).

Results and Discussion

I. **Size-Monodisperse Unmodified Silver Nanocrystals.** The TEM image of Ag-**1**, reproduced in Figure 1, reveals that the dodecane thiol capped silver nanocrystals are spherical, near size-monodisperse, and self-assemble to form a hexagonally close-packed array. An analysis of 200 nanocrystals indicates that the average diameter of the Ag nanocrystal core is 73 ± 4 Å, corresponding to a polydispersity of 1.07.

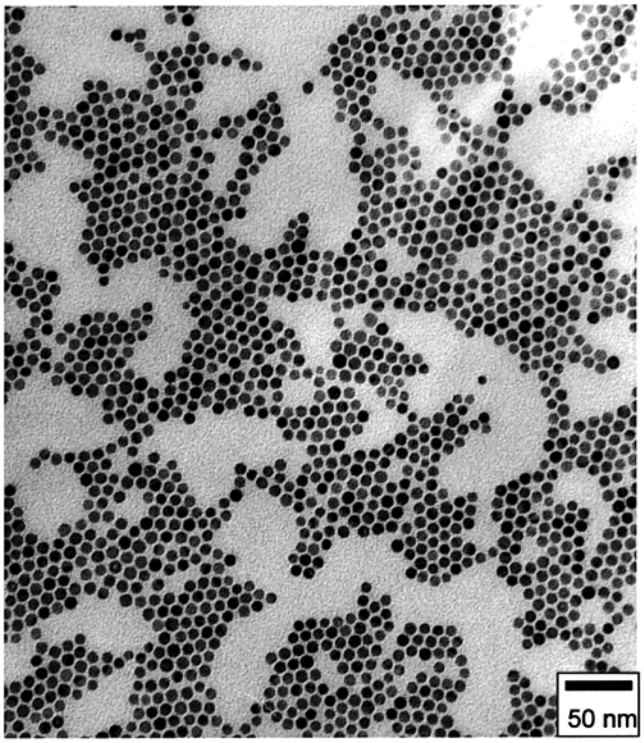


Figure 1. TEM of near size-monodisperse Ag nanocrystals stabilized by a chemisorbed monolayer of **1**, Ag-**1**.

A comparison of the ^{1}H NMR spectra (not shown) of **1** in solution and of **1** adsorbed at the surface of a Ag nanocrystal in Ag-**1** reveals that the resonances assigned to the methylene protons α (δ 2.52 quartet) and β (δ 1.61 multiplet) to the thiol moiety are broadened to the extent that they are no longer visible in Ag-**1**.[27] This line broadening, which results from both the discontinuity in the diamagnetic susceptibility of the silver-hydrocarbon interface and the residual dipolar interactions in the layer on account of spatial constraints,[31] confirms that all of **1** is chemisorbed at the surface of a silver nanocrystal.

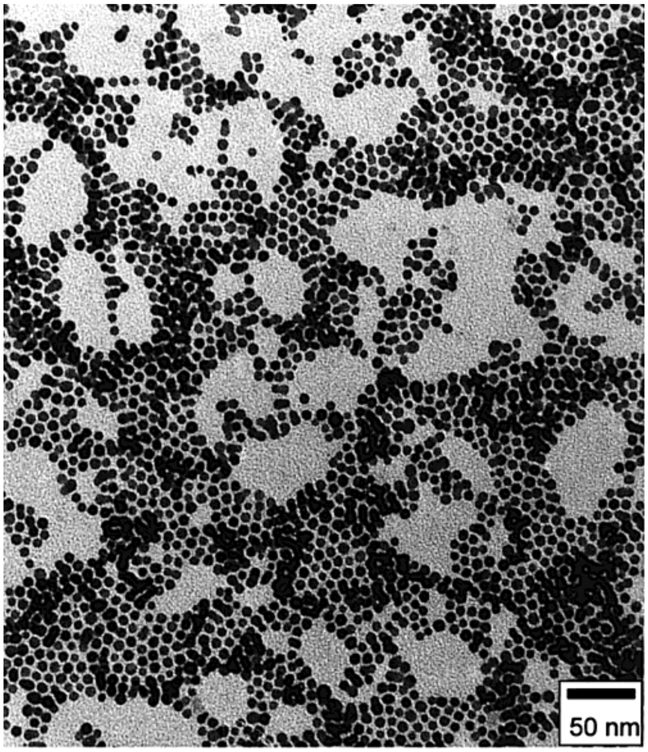


Figure 2. TEM of near size-monodisperse Ag nanocrystals stabilized by a chemisorbed monolayer of **1** (85%) and **2** (15%), Ag-**2**.

Elemental analysis of Ag-**1** reveals that the thiol adsorbed at the surface of the Ag nanocrystals accounts for 17.7% of their mass.[27] Assuming that each nanocrystal is covered by a monolayer of **1**, it has been calculated that there are an average of 1316 molecules adsorbed at the surface of each nanocrystal and that each molecule occupies 13 Å^2 of the available surface area. This area is less than the established one of 17.5 Å^2 expected for a monolayer of **1** self-assembled at a flat silver surface,[30] a finding that can be accounted for by the extreme curvature of the surface of the silver nanocrystal.

II. Size-Monodisperse Modified Silver Nanocrystals. One possible route to preparing Ag-**2** is to prepare silver nanocrystals in the presence of a mixture of **1** and **2**. However, nucleation of nanocrystals in the presence of a mixture of thiols generally leads to irregularly shaped clusters that are not amenable to size-selective precipitation.[28] As a consequence, the approach adopted was similar to that developed by Murray and co-workers, i.e., surface-exchange between an adsorbed thiol and a thiol incorporating a binding site in solution.[28]

The TEM image reproduced in Figure 2 demonstrates that modification of Ag-**1** to form Ag-**2** does not result in a significant change in the diameter or the degree of polydispersity of the silver nanocrystals. Specifically, an analysis of 200 nanocrystals yields an average diameter for the silver nanocrystal core of 73 ± 8 Å and a polydispersity of 1.09. These values agree well with those obtained for Ag-**1**.

The data obtained from analysis of TEM images show that modification of silver nanocrystals has not significantly altered their size indicating that Ag-**2** can be visualized as being similar to Ag-**1** except for the variation in capping ligands.

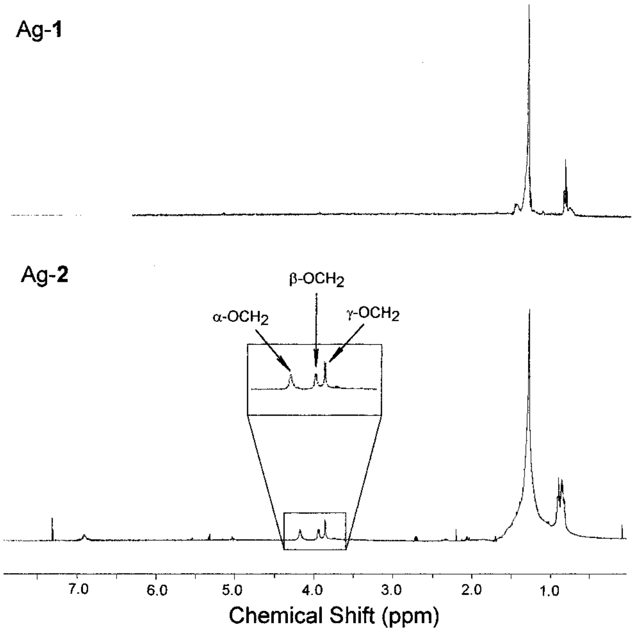


Figure 3. (a) ^{1}H NMR spectrum of Ag-**1** in $CDCl_3$. (b) ^{1}H NMR spectrum of Ag-**2** in $CDCl_3$. Expanded region shows α-, β-, and γ-methyleneoxy resonances of the dibenzo-24-crown-8 macrocycle.

The absence of a resonance in the ^{1}H NMR spectrum of Ag-**2** (Figure 3) that can be assigned to the protons of the methylene groups α, β, or γ to the thiol moieties of either **1** or **2** confirms that these molecules are chemisorbed at the surface of the Ag nanocrystal.[29] The presence of broadened resonances that can be assigned to the α-, β-, and γ-methyleneoxy resonances of the crown-ether moiety further confirms the presence of **2** at the surface of the Ag nanocrystal. The broadening of these resonances is most likely a result of the restricted motion of **2**.[31]

The degree of exchange, determined from the ratio of integrals of the terminal methyl proton resonances of **1** and the collective α-, β-, and γ-methyleneoxy protons of **2**, is 15% for Ag-**2**. Elemental analysis estimates[29] the organic composition to be 17.6%. Assuming the nanocrystals are spherical and covered by a monolayer of **1** and **2**, it has been calculated that each nanocrystal is covered by an average of 1015 thiol molecules (152 molecules of **2**, assuming 15% coverage as determined from the ^{1}H NMR spectrum) and that each thiol occupies on average 17 Å^2 of the available surface area.[30] This value is significantly larger than that for Ag-**1** due, possibly, to the steric bulk associated with the dibenzo-24-crown-8 moiety.

III. Recognition-Directed Aggregation of Modified Silver Nanocrystals in Solution. It has been shown[22] that the dibenzylammonium cation **4** is recognized and bound by the dibenzo-24-crown-8 moiety incorporated at the terminal position of the dodecane thiol, **2**, chemisorbed at the surface of a gold nanocrystal (Scheme 1). As **4** contains only one binding site, however, this recognition event does not lead to aggregation of Ag-**2**.

In the case of the bis-dibenzylammonium dication **3**, there is the possibility of bridging two Ag-**2** and of aggregation (Scheme 2). For this possibility to be realized, however, it is necessary that **3** is also recognized and bound by Ag-**2**. Accordingly, high-resolution ^{1}H NMR spectroscopy was used to characterize the interactions at a molecular level between **2** and **3**.

Shown in Figure 4a are partial ^{1}H NMR spectra of **2**, **3**, and a 2:1 mixture of **2** and **3**, denoted (**2**+**3**+**2**) in $CDCl_3$:CD_3CN (4:1, v/v). Consistent with previously reported findings,[23−25] uncomplexed **2** exhibits resonances at δ 4.14, 3.92, and 3.84 that are assigned to the α-, β-, and γ-methyleneoxy protons of the dibenzo-24-crown-8 moiety, respectively. Likewise, un-

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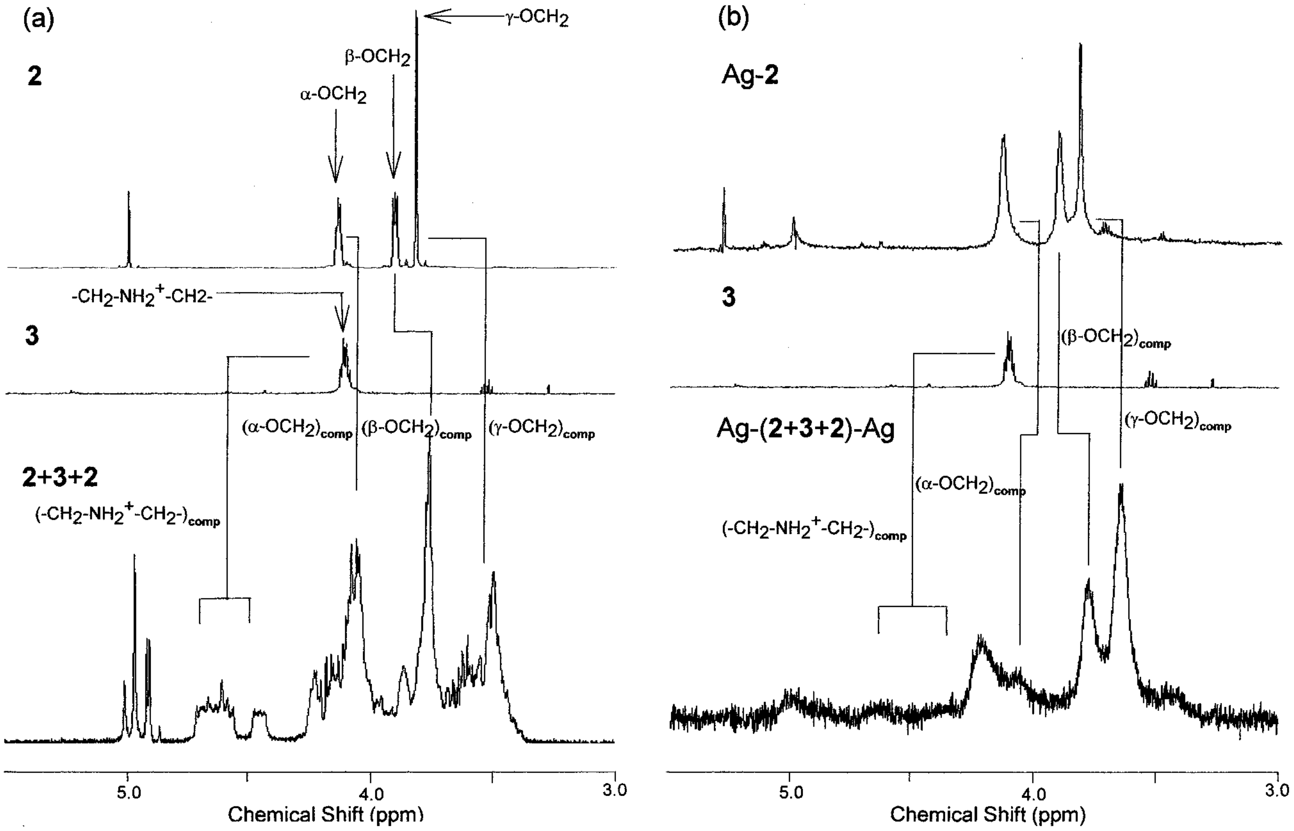


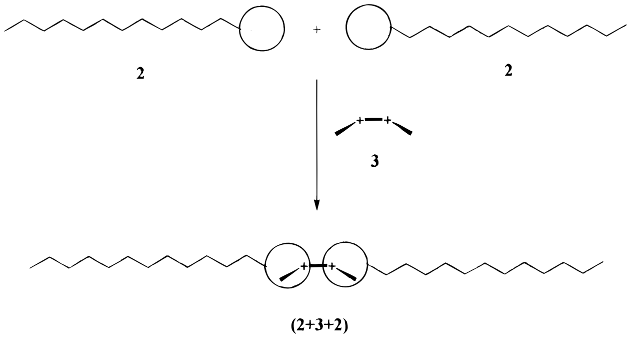
Figure 4. (a) Partial ^{1}H NMR spectra of **2**, **3**, and a 2:1 mixture of **2** and **3**. (b) ^{1}H NMR spectra of Ag-**2**, **3**, and a 2(with respect to **2**):1 mixture of Ag-**2** and **3**.

complexed **3** exhibits a resonance at δ 4.14 that is assigned to the methylene protons α to the NH_2^+ centers. Also consistent with previously reported findings,[33] a 2:1 mixture of **2** and **3** exhibits four sets of resonances which can be assigned to uncomplexed **2** and **3** and to complexed (**2**+**3**) and (**2**+**3**+**2**). Specifically, in the case of the 2:1 complex of **2** and **3**, the resonances assigned to the α-, β-, and γ-methyleneoxy protons of **2** are shifted upfield by δ 0.12, 0.17, and 0.26 to δ 4.02, 3.75, and 3.58, respectively, and are split. In addition, the resonances assigned to the methylene protons α to the NH_2^+ centers in **3** are shifted downfield to δ 4.50 and are also split. These spectra are consistent with the asymmetry of the dibenzo-24-crown-8 moieties of **2** and the methylene groups of **3** in (**2**+**3**+**2**) and with the palindromic-like symmetry of (**2**+**3**+**2**). On this basis, it is concluded that **2** and **3** form the 2:1 pseudorotaxane complex shown in Scheme 4.

Having used high-resolution ^{1}H NMR spectroscopy to establish that **3** is recognized and bound by **2** in solution, it was then necessary to establish that complexes analogous to those formed between **2** and **3**, namely (**2**+**3**) and (**2**+**3**+**2**), are also formed between **2** and **3** when **2** is adsorbed at the surface of an Ag nanocrystal. Accordingly, high-resolution ^{1}H NMR spectroscopy was used to characterize the interactions at a molecular level between Ag-**2** and **3**.

Shown in Figure 4b are ^{1}H NMR spectra of Ag-**2**, **3**, and a 2:1 mixture of Ag-**2** and **3**, denoted Ag-(**2**+**3**+**2**)-Ag in $CDCl_3$:CD_3CN (4:1, v/v). As expected, Ag-**2** exhibits broadened resonances at δ 4.14, 3.92, and 3.84 that are assigned to the α-, β-, and γ-methyleneoxy protons, respectively. Consistent with the findings reported above, a 2:1 mixture of Ag-**2** and **3** exhibits resonances which are assigned to uncomplexed Ag-**2** and **3**. There are also resonances which are tentatively assigned to complexed Ag-(**2**+**3**) and Ag-(**2**+**3**+**2**)-Ag, specifically, broadened resonances assigned to the α-, β-, and γ-OCH_2 protons of Ag-**2** that are shifted upfield by δ 0.1, 0.2, and 0.2 to δ 4.0, 3.8, and 3.6, respectively, and are split. Also, broadened resonances assigned to the methylene protons α to the NH_2^+ centers in **3** are shifted downfield to δ 4.5 and are also split. It should be noted that it is possible there is a contribution to the measured spectrum by bis-dibenzylammonium dications that are bound by two dibenzo-24-crown-8 sites on the surface of the same Ag nanocrystal. It should also be noted, however, that this interaction will not lead to aggregation of these nanocrystals.

Scheme 4. The [3]Pseudorotaxane, (**2**+**3**+**2**), Formed by **2** and **3**



Although the difficulty in obtaining a highly resolved ^{1}H NMR spectrum of what is essentially an aggregating colloid cannot be overstated, it may be concluded from the above that Ag-**2** and **3** form the [3]pseudorotaxane complex shown in

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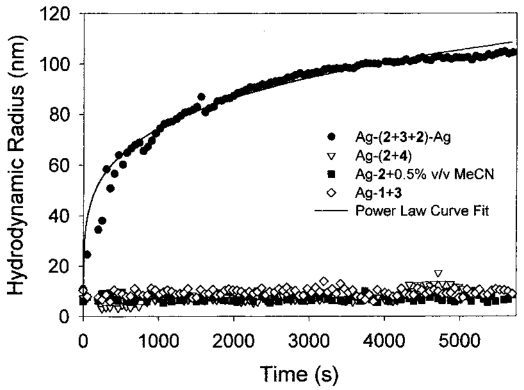

Figure 5. DLS profile of Ag-**2** prior to and following addition of **3**. Also plotted are DLS profiles for the indicated controls. A curve-fitting based on a least-squares method, using a power-law model, resulted in a correlation coefficient, R^2, of 0.96.

Scheme 2. However, it is not possible to determine accurately the extent of complexation.

IV. **Recognition-Induced Aggregation of Modified Silver Nanocrystals.** Having shown that the addition of **3** to a dispersion of Ag-**2** results in the formation of a complex which links two nanocrystals, namely Ag-(**2**+**3**+**2**)-Ag, the question which arises is, does this lead to the formation of larger nanocrystal aggregates in solution?

Shown in Figure 5 are DLS measurements made following addition of **3**, dissolved in MeCN, to Ag-**2** dispersed in $CHCl_3$ (2:1 ratio of **2** and **3**). It is clear from these measurements that addition of **3** is followed by a growth in the hydrodynamic radius of the scattering entity which, based on the findings reported above, is assumed to be silver nanocrystal aggregates of the type shown in Scheme 2. The growth of the aggregate in solution is power-law in nature and suggests strongly that aggregation is diffusion-limited and that the aggregates formed are open fractal structures.[34]

A series of control experiments were performed and included the following: addition of **3**, dissolved in MeCN, to Ag-**1** dispersed in $CHCl_3$ (8:1 ratio of **1** and **3**); addition of **4**, dissolved in MeCN, to Ag-**2** dispersed in $CHCl_3$ (1:1 ratio of **2** and **4**); and addition of MeCN to Ag-**2** dispersed in $CHCl_3$. The results of these experiments are also plotted in Figure 5. On the basis of these control experiments, it is concluded that nanocrystal aggregation is observed *only* when dibenzo-24-crown-8 moieties are present at the surface of the silver nanocrystal and when the bis-dibenzylammonium dication is present in solution.

V. **Inhibition of Recognition-Induced Aggregation of Modified Silver Nanocrystals.** If pseudorotaxane formation is driving aggregation then it would be expected that aggregation of Ag-**2** (in the presence of added **3)** would be inhibited by addition of an excess of either **4** or **5**. In the case of addition of an excess of **4**, the available binding sites on the surface of Ag-**2** will be occupied and, therefore, incapable of binding to another Ag-**2**. In the case of addition of an excess of **5**, the unbound **3** present in solution will be complexed and will no longer be able to participate in nanocrystal aggregation.

Shown in Figure 6 is the effect of addition of **4** and **5** to an aggregating colloid of Ag-**2**. It is clear that the above expectations are justified and, furthermore, that complete inhibition of further growth occurs after addition and for the remaining period of observation.

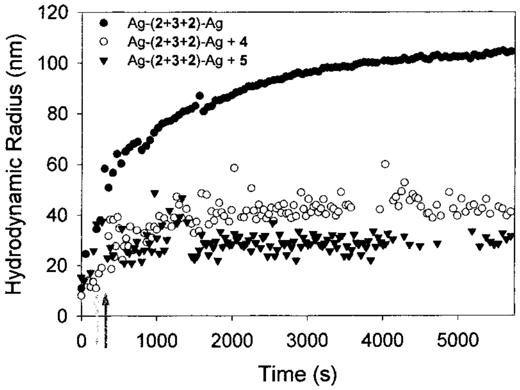

Figure 6. DLS profiles of Ag-**2**, prior to and following addition of **3**. Also plotted are DLS profiles prior to and following addition of **3** and subsequent addition of **4** or **5**. The arrows indicate the time of addition of **4** (dark grey) and **5** (light grey).

Since pseudorotaxane formation between the molecular components, **2** and **3**, is a molecular interaction, it occurs on a time-scale shorter than that for pseudorotaxane-driven nanocrystal aggregation between Ag-**2** and **3**. This is evidenced by the rapid quenching of further growth upon addition of inhibiting compounds, i.e., a reaction where rate is dependent on diffusion of molecules to binding sites situated on nanocrystals. In contrast, nanocrystal aggregation relies on the diffusion of nanocrystals in the correct orientation and state and, therefore, does not occur at the same rate. This differentiating feature is expected to characterize recognition-driven nanocrystal assembly processes when the initiator for aggregation is a molecular-level recognition event. Furthermore, the ability to control the extent of aggregation is a novel feature and points toward future developments in controlling nanocrystal assembly.

Conclusions

The preparation and characterization of near monodisperse silver nanocrystals stabilized by chemisorption of a mixture of an alkane thiol (85%) and an alkane thiol incorporating a dibenzo-24-crown-8 moiety (15%) has been described. It has been shown that nanocrystal aggregation is initiated by addition of a bis-dibenzylammonium dication, a molecule with the ability to recognize and bind with two dibenzo-24-crown-8 moieties on two different silver nanocrystals. Aggregation leads to growth of a fractal structure in solution, the kinetics of growth being described by a power law model. Furthermore, control over nanocrystal assembly has been demonstrated in that addition of excess of the receptor or of the substrate inhibits aggregation. The insights gained in this work, coupled with a detailed understanding of the mechanism of nanocrystal aggregation, are essential for the self-assembly of complex nanocrystal architectures in solution or on technologically relevant substrates.

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Supporting Information Available: Histograms for this material is available free of charge via the Internet at http://pubs.acs.org. Figures 1 and 2 in the text (PDF).

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