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Programmed Assembly of Binary Nanostructures in Solution

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Near size-monodisperse silver nanocrystals and silica nanospheres have been prepared and surface-modified with the [2]pseudorotaxane recognition motifs, dibenzo[24]crown-8 and dibenzylammonium cation, respectively. The silver nanocrystals, 7 nm in diameter, are shown to recognize and bind to the silica nanospheres, 180 nm in diameter, via pseudorotaxane formation. The result is the templated assembly of silver nanocrystals at the surface of the larger silica nanosphere core. This composite material exhibits optical properties that are a consequence of localizing silver nanocrystals at the surface of the silica nanospheres. The templating process is also shown to be reversible. This noncovalent recognition-directed templating strategy represents a novel metallization process resulting in the formation of composite media whose collective properties can be controlled.

Introduction

Motivated by the prediction that existing microfabrication techniques will reach a lower size limit soon, new approaches to arranging conducting, semiconducting and nonconducting materials on the nanoscale are of growing interest.[1,2] Recently, size-monodisperse nanocrystals of a wide range of materials have been prepared and their size-dependent electronic and magnetic properties studied.[3,4] However, it is the collective electronic and magnetic properties of organized assemblies of size-monodisperse nanocrystals that are increasingly the subjects of investigation.[5] Although many studies deal with assemblies of single nanocrystals few studies focus on assemblies of two (binary) or more types of nanocrystals.[6−9]

Recently, we have reported 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 [10]. These nanocrystals were shown to recognize, and bind selectively in solution, a dibenzylammonium cation, forming a [2]pseudorotaxane coated nanocrystal.

Most recently, we have demonstrated the recognition-directed assembly of silver nanocrystals in solution via pseudorotaxane formation.[11] Specifically, a thiol modified dibenzo[24]crown-8 recognition motif was covalently linked to the surface of 7 nm diameter silver nanocrystals. Upon addition of bis-dibenzylammonium dication, aggregation of nanocrystals was observed. We further demonstrated inhibition of the aggregation phenomenon by addition of either an excess of dibenzo[24]crown-8 or dibenzylammonium cation recognition motifs.

In this paper, we describe, for the first time, the formation of a binary nanostructure in solution consisting of a silica nanosphere that behaves as a core for the noncovalent recognition-directed templated assembly of a silver nanocrystal shell. Recent work has outlined the use of non-specific electrostatic effects to assemble multilayers of nanoparticles onto polystyrene latex templates. The use of a molecular recognition process, which is specific in nature, driving a templating process has not been previously reported.

Unique to this system are the molecular components that drive the assembly process. The recognition and selective binding of dibenzo[24]crown-8 and dibenzylammonium salt to form a [2]-pseudorotaxane is a well-developed supramolecular system (Scheme 1).[12,13] Accordingly, we covalently link dibenzo[24]-crown-8 to the surface of silver nanocrystals using thiol surface groups and a precursor of dibenzylammonium cation to the surface of silica nanospheres using a silane coupling agent. The dibenzylammonium cation is subsequently generated in situ by photolysis of the precursor. These recognition motifs were expected to interact to form a [2]pseudorotaxane between the silica and silver surfaces resulting in the formation of a silica/silver composite material (Scheme 2). Hence, the recognition-directed or programmed assembly of a binary nanostructure ought to be possible.

Experimental Section

Non-Photoactive Stabilizers. All compounds were characterized using elemental analysis and ^{1}H NMR spectroscopy. ^{1}H NMR spectra were recorded using either Varian 300 MHz FT-NMR or Varian 500 MHz FT-NMR spectrometers with either the solvent reference or TMS as the internal standard. All chemical shifts are quoted on the δ scale. All coupling constants are expressed in Hertz. Dispersions and solutions used in ^{1}H NMR spectroscopic studies were prepared from dry samples of the desired nanocrystal or compound by addition of the appropriate deuterated solvent.

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 onto a carbon-coated copper grid. UV−vis spectroscopy was performed using a HP-8452A Spectrophotometer using LabView software written to acquire data. All UV−vis spectra were referenced using appropriate solution backgrounds.

Chemicals including dodecane thiol, **1**, were purchased from Aldrich and used without further purification. Dodecane thiol-modifed dibenzo[24]crown-8, **2**, was prepared as described

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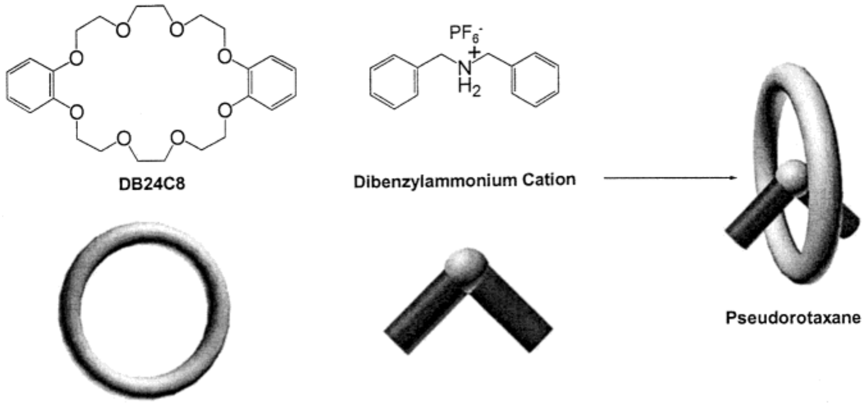
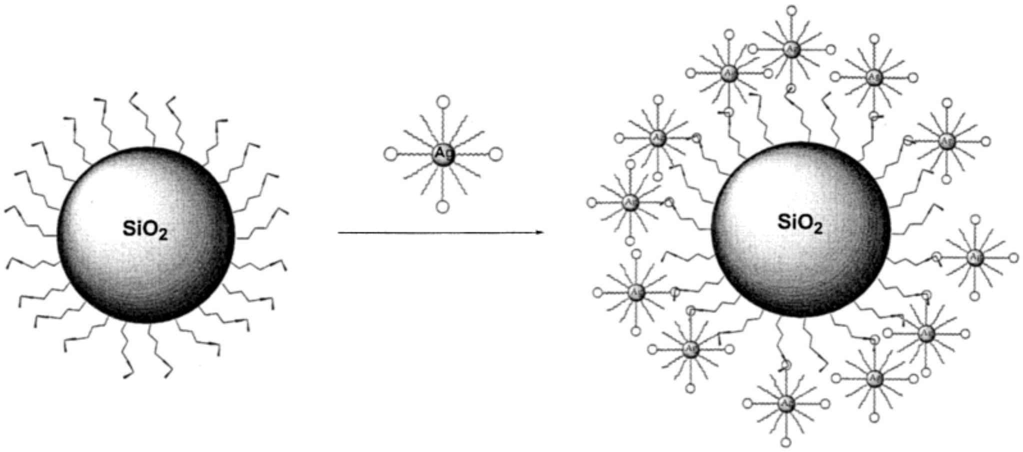
SCHEME 1: [2]Pseudorotaxane Formation in this System is Devolved from a Recognition and Selective Binding of Dibenzo[24]crown-8 and Dibenzylammonium Salt. This Recognition Process is the Basis of the Templated Assembly of Silver Nanocrystals and Silica Nanospheres Discussed in this Paper.



SCHEME 2: Strategy for Assembling Templated Silver Nanocrystals on Silica Nanospheres. Each Silver Nanocrystal has a Population of Dibenzo[24]crown-8 Recognition Motifs Covalently Linked to its Surface and Each Silica Nanosphere has a Near-Monolayer Coverage of Dibenzylammonium Recognition Motifs at its Surface. These Recognition Motifs Interact to Form a [2]Pseduorotaxane which Results in the Assembly of Silver Nanocrystals around the Silica Nanosphere.



previously.[10] Anhydrous solvents, where used, were purchased from Aldrich and used within 1 week.

1: ^{1}H NMR (CDCl$_3$): δ 0.88 (t, 3H, $J = 7.0$ Hz); δ 1.22 (m, 16H); δ 1.36 (m, 2H); δ 1.61 (m, 2H); δ 2.52 (q, 2H, $J = 7.0$ Hz, $J = 3.5$ Hz); $C_{12}H_{26}S$ (202.07): calcd C 71.21, H 12.95, S 15.89; found C 71.19, H 13.12, S 15.55.

2: ^{1}H NMR (CDCl$_3$): δ 1.27 (m, 12H); δ 1.39 (m, 2H); δ 1.61 (m, 2H); δ 2.32 (t, 2H, $J = 7.0$ Hz); δ 2.52 (q, 2H, $J = 7.0$ Hz, $J = 3.5$ Hz); δ 3.82−3.85 (m, 8H); δ 3.89−3.97 (m, 8H); δ 4.12−4.24 (m, 8H); δ 5.04 (s, 2H); δ 6.85−6.95 (m, 7H); $C_{36}H_{54}O_{10}S$ (678.87): calcd C 64.25, H 7.96; found C 63.8, H 7.86.

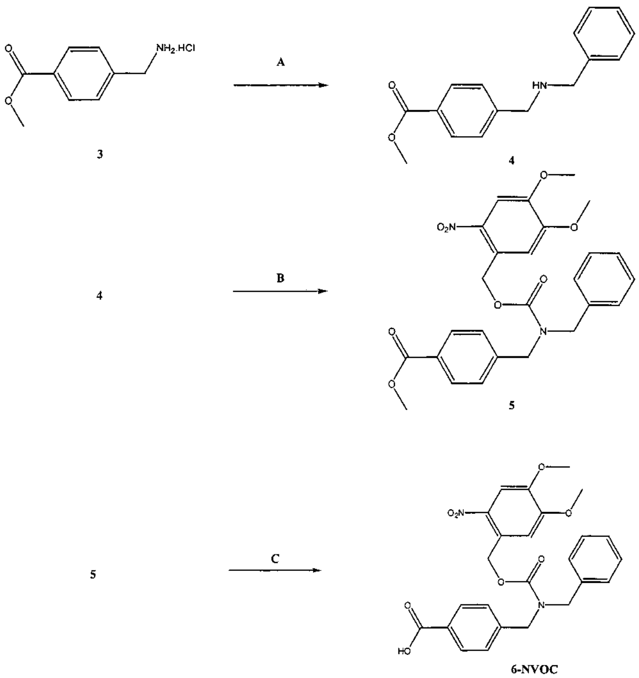
Photoactive Molecular Stabilizer Precursors. The photoactive molecular component was prepared according to Scheme 3. All reactions involving NVOC were carried out in flasks protected from external light sources.

4: 4-carbomethoxydibenzylamine. Methyl aminomethylbenzoate hydrochloride, **3** (1.12 g, 6.0 mmol), was transformed into the free base by washing with 5% Na_2CO_3 aqueous solution (200 mL) followed by extraction using $CHCl_3$ (3 × 100 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated to afford 0.60 g (67%) of methyl aminomethylbenzoate. A solution of methyl aminomethylbenzoate (0.60 g, 4 mmol) and benzaldehyde (0.42 g, 4 mmol) in PhMe was heated under reflux for 3 h, whereas the H_2O discharged was isolated with a Dean−Stark separator. The solution was evaporated under reduced pressure to yield 1.02 g (100%) of 4-carbomethoxybenzylidenebenzylamine as a pale yellow oil [^{1}H NMR (CDCl$_3$): δ 3.83 (s, 3H), δ 4.80 (s, 2H), δ 7.33−7.37 (m, 5H), δ 7.70−7.74 (m, 2H), δ 7.93−7.96 (d, 2H), δ 8.34 (s, 1H)] which was dissolved in a THF/MeOH (1:1, 100 mL) solution. $NaBH_4$ (0.15 g, 4 mmol) was added with stirring at room temperature. A further portion of $NaBH_4$ (0.15 g, 4 mmol) was added to the reaction mixture after an additional 2 h. The solution was stirred subsequently for 20 h, before being evaporated under reduced pressure. The residue was partitioned between H_2O (100 mL) and EtOAc (100 mL). The aqueous phase was then further extracted with EtOAc (2 × 100 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated to afford 0.96 g (94%) of **4** as a pale white oil.

4: ^{1}H NMR (CDCl$_3$): δ 3.84 (s, 3H), δ 3.89 (s, 2H), δ 3.94 (s, 2H), δ 7.24−7.32 (m, 2H), δ 7.35−7.37 (m, 3H), δ 7.43−7.49 (m, 2H), δ 8.00−8.10 (d, 2H).

5: N−(4-carbomethoxydibenzylamine)carbamate NVOC. 6-nitroveratryloxy chloroformate (NVOC) (1.06 g, 4 mmol) was added with stirring to a solution of **4** (0.96 g, 3.8 mmol) and $NaHCO_3$ (0.34 g, 4 mmol) in $CHCl_3/Et_2O$ (9:1, 100 mL) at 5 °C. The solution was stirred for 2 h, before being treated with saturated aqueous $NaHCO_3$ (1 × 100 mL) and H_2O (2 × 100 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated to afford the crude title compound. The crude

SCHEME 3: Synthetic Strategy used to Obtain 6-NVOC. Reagents and Conditions: A. (1) $Na_2CO_{3(aq)}$ (2) Benzaldehyde, Toluene, 140 °C, 3h (3) $NaBH_4$, MeOH/THF, RT, 20h. B. NVOC, $NaHCO_3$, $CHCl_3/Et_2O$, 5 °C, 2 h. C. 3M $NaOH_{(aq)}$, MeOH/THF, RT, 3 h.



product was chromatographed (SiO_2: EtOAc/hexane, 50:50) to yield 1.74 g (92%) of 5 as a yellow oil.

5: ^1H NMR ($CDCl_3$): δ 3.69 (br s, 3H), δ 3.94 (s, 3H), δ 3.97 (s, 3H), δ 4.56−4.59 (br d, 4H), δ 5.68 (br s, 2H), δ 6.87−6.90 (br d, 1H), δ 7.21−7.39 (br m, 7H), δ 7.72 (s, 1H), δ 7.98−8.05 (d, 2H).

6-NVOC: N−(4-carboxydibenzylamine)carbamate NVOC. 50 mL of a 6M NaOH aqueous solution was added dropwise to a stirred solution of **5** (1.74 g, 3.5 mmol) in THF/MeOH (1:1, 50 mL) at ambient temperature for 3 h. The resulting solution was evaporated under reduced pressure and the residue was collected and partitioned between 2M HCl (100 mL) and EtOAc (100 mL). The aqueous phase was further extracted with EtOAc (2 × 100 mL) and the combined organic extracts were dried ($MgSO_4$), filtered, and concentrated. Recrystallization from EtOH yielded 1.41 g (84%) of **6-NVOC** as a fine yellow powder.

6-NVOC: ^1H NMR ($CDCl_3$): δ 3.69 (br s, 3H), δ 3.97 (s, 3H), δ 4.56−4.61 (br d, 4H), δ 5.69 (br s, 2H), δ 6.88−6.91 (br d, 1H), δ 7.21−7.39 (br m, 7H), δ 7.72 (s, 1H), δ 7.98−8.05 (d, 2H); $C_{25}H_{24}N_2O_8$ (480.47): calcd C 62.49, H 5.03, N 5.83; found C 61.82, H 4.82, N 5.74.

Preparation of Modified Silver Nanocrystals and Silica Nanospheres. Silver nanocrystals were prepared using a modified two-phase synthesis procedure originally introduced by Brust et al.[2,14] These nanocrystals were size-selected to isolate near size-monodisperse fractions, which were subsequently modified with a long-chain thiol incorporating a dibenzo[24]-crown-8 recognition motif using previously published methods.[11] These silver nanocrystals are denoted as Ag-**2**.

Silica nanospheres, 180 nm in diameter, were synthesized according to methods originally developed by Stöber et al.[15] and subsequently modified by van Blaaderen and Vrij.[16] Modification of silica surfaces using alkoxysilanes is a well-established method for preparing hydrophobic silica. Here, we prepared aminopropyl functionalized silica nanospheres using 3-aminopropyldimethylethoxysilane as a silane-coupling agent. Solid-phase organic synthetic methods were used to couple the photoactive molecular component, **6-NVOC**, to the amine-modified nanospheres.[19] Specifically, to a dispersion of amine-modified silica (2.42×10^{15} nanospheres dm^{-3}, 7×10^{-4} mol $NH_{2(surface)}$ dm^{-3}) in anhydrous CH_2Cl_2 was added **6-NVOC** (0.07 g, 1.4×10^{-4} mol) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDAC) (0.03 g, 1.4×10^{-4} mol) and the mixture was stirred for 24 h at ambient temperature. The dispersion was then centrifuged (3000 rpm, 5 min; Sorvall Instruments RT6000B using A500 rotor) and sonicated (Ultrawave, 15 min) consecutively from alternating MeOH (50 mL) and $CHCl_3$ (50 mL) washing solvents five times.

An experiment has also been performed whereby amine-modified silica nanospheres and **6-NVOC** have been mixed in precisely the same manner as described in the manuscript but in the *absence* of any coupling agent namely, EDAC. Subsequent centrifugation cycles and analysis by UV−vis spectroscopy was performed to determine the absence or otherwise of **6-NVOC** at the surface of the silica nanonspheres.

These modified nanospheres, referred to as SiO_2-(**6-NVOC**) were characterized by transmission electron microscopy (TEM) and UV−vis spectroscopy.

Transmission electron microscopy (TEM) was used to obtain information relating to the size of both silver nanocrystals and silica nanospheres. UV−vis spectroscopy was used to confirm the presence of **6-NVOC** at the surface of silica nanospheres.

Photoactivation of Modified Silica Nanospheres. The 355 nm line of a Continuum Surelite Nd:YAG laser was used as the light source in all photoactivation experiments. The output from the laser was measured to be 170 mW/cm^2. Briefly, 2 mL of a chloroformic dispersion of SiO_2-(**6-NVOC**) (2.42×10^{15} nanospheres dm^{-3}) was placed in a glass cuvette and stirred for a period of 1 h at room temperature while being irradiated. The photoactivated nanospheres were then centrifuged (3000 rpm, 3 min) and washed using chloroform (20 mL) five times.

These photoactivated nanospheres, referred to as SiO_2-**6**, were characterized using UV−vis spectroscopy and TEM.

The dibenzylamine-modified nanospheres were converted to their dibenzylammonium salts by addition of hexafluorophosphoric acid to a 2 mL methanolic dispersion of SiO_2-**6** (2.42×10^{15} nanospheres dm^{-3}) until a pH of 1 was obtained. The dispersion was then stirred for 2 h, after which time the nanospheres were centrifuged (3000 rpm, 3 min) and washed using methanol (20 mL) five times followed by a further two washings in chloroform (20 mL). After the final washing the nanospheres were redispersed in chloroform. These dibenzylammonium-modified spheres are referred to as SiO_2-**6**+.

Programmed Assembly of Binary Nanostructures in Solution. Using particle size data obtained from TEM, an estimation of the number of silver nanocrystals (approximated as discs) required to coat a single silica nanosphere (approximated as spheres) was made. On the basis of this estimation, a ratio of 2640 silver nanocrystals/silica nanosphere was used in all experiments as representative of complete coverage of silica. A typical experiment resulting in the formation of binary nanostructures involved the addition of 100 μL of a chloroformic dispersion of Ag-**2** (1.11×10^{18} nanocrystals dm^{-3}) to a 300 μL chloroformic dispersion of SiO_2-**6**+ (1.38×10^{14} nanospheres dm^{-3}). Samples for TEM were prepared after 24-hour equilibration. Relevant control experiments were also performed: these involved mixing similar ratios of silver nanocrystals and silica nanospheres where either one

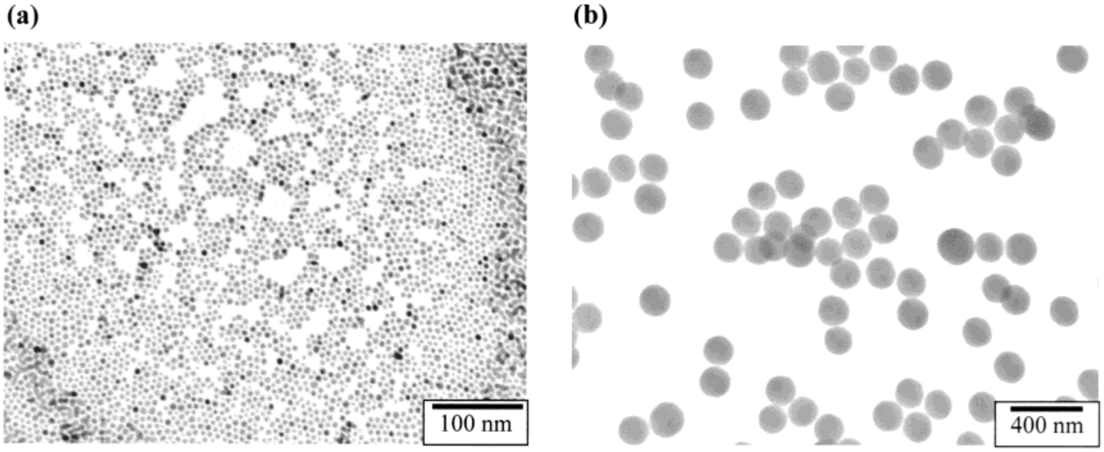


Figure 1. (a) Size monodisperse silver nanocrystals, Ag-**2**, where the stabilizing ligands constitute dodecane thiol incorporating a dibenzo[24]-crown-8 motif (15%) and dodecane thiol (85%). The nanocrystals crystallize to hexagonally close-packed arrays and have a polydispersity number of 1.09. (b) Size monodisperse silica nanospheres, SiO_2-(**6-NVOC**). These nanospheres are readily dispersed in organic solvents and have a polydispersity number of 1.08.

or both recognition motifs were absent. To support the assertion that a^{2}pseudorotaxane is being formed at the interface between silver nanocrystals and silica nanospheres, an excess of dibenzo^{24}-crown-8 (0.02 g, 1.12×10^{-4} mol) was added to a 300 μL chloroformic dispersion of **SiO_2-6+** (1.38×10^{14} nanospheres dm^{-3}, approximately 1.12×10^{-8} mol **6**+) thereby saturating all dibenzylammonium binding sites at the surface of the nanospheres. Within minutes, 100 μL of a chloroformic dispersion of Ag-**2** (1.11×10^{18} nanocrystals dm^{-3}) was added to the sample. These conditions are expected to inhibit binding of Ag-**2** to SiO_2-**6**+.

All binary nanostructures were characterized using TEM and UV−vis spectroscopy. Prior to characterization, each sample was centrifuged (3000 rpm, 3 min) and the precipitate redispersed in 400 μL of $CHCl_3$. Analysis was performed on this isolated fraction only. UV−vis spectra are presented as normalized spectra (uncorrected for scattering).

Reversal of Programmed Assembly of Binary Nanostructures in Solution. Realizing that the [2]pseudorotaxane used in this study is formed between a dibenzylammonium salt and dibenzo[24]crown-8, it should be possible to reverse the assembly of silver nanocrystals on silica nanospheres by addition of a base, in this case triethylamine. This is expected to deprotonate the dibenzylammonium salt and convert it into a dibenzylamine moiety which has no interaction with dibenzo[24]crown-8. To demonstrate this feature, an excess of triethylamine (0.02 g, 1.98×10^{-4} mol) was added to the dispersion, described above, of Ag-**2** and SiO_2-**6**+ and was left to equilibrate for 24 h.

Reversal of the templated assembly of binary nanostructures was characterized using TEM and UV−vis spectroscopy. Again, prior to characterization the sample was centrifuged (3000 rpm, 3 min) and redispersed in 400 μL of $CHCl_3$ for analysis. UV−vis spectra are presented as normalized spectra (uncorrected for scattering).

Thermal Processing of Templated Binary Nanostructures. To fabricate robust architecture from nanocrystal assemblies it will be important to develop facile methods to fix the assembled components and thus eliminate the possibility for disassembly. In this context, a sample of the binary nanostructure obtained from mixing Ag-**2** and SiO_2-**6**+ was placed in an oven and heated (Carbolite furnace fitted with a Eurotherm controller) from 150 °C to 300 °C in 50 °C increments over a period of 20 min. The resultant assembly was characterized using TEM.

Results and Discussion

Hydrophobic monodisperse silica nanospheres have been prepared using traditional methods.[16] It is noted that the synthesis of silica nanospheres does not permit complete coverage of amine groups at the surface of the nanospheres.[17,18] However, when coupling **6-NVOC** to amine-modified silica nanospheres monolayer coverage of amine termini was assumed. Established techniques from solid-phase synthesis have been used to couple the surface amine termini with photoprotected dibenzylamine moieties, **6-NVOC**. Using UV−vis spectroscopy, we have been able to quantify the number of **6-NVOC** molecules at the surface of the silica nanospheres and this was determined to be 1.61×10^4 **6-NVOC** per nanosphere. Both the coupling strategy employed and the photoprotecting group used are known and practiced in the literature.[19,20]

To determine if the coupling strategy used in this work was effective, an attempted synthesis whereby the coupling agent, EDAC, was absent was performed. The absence of any absorption trace representing **6-NVOC** at the surface of the silica nanospheres indicates that a coupling agent is necessary to couple **6-NVOC** covalently to the surface of the nanospheres and no non-specific interactions lead to the UV−vis spectra presented in Figure 2a.

After surface modification with **6-NVOC**, the UV−vis spectrum of SiO_2-(**6-NVOC**) reveals the presence of **6-NVOC** at the surface of the nanospheres (Figure 2a). Furthermore, after photolysis of this precursor, using laser light, it is equally clear that the photoactive component has been removed, whereas the dibenzylamine group still resides at the surface of the nanospheres (Figure 2b). Care has been taken here not to use wavelengths below 355 nm as these may lead to degradation of the dibenzylamine groups. Protonation of SiO_2-**6** converts the free dibenzylamine to its corresponding hexafluorophosphate dibenzylammonium salt. Salts of this nature are typically found to be insoluble in chloroformic solvents; however, we have found that when **6**+ is chemisorbed on the surface of silica nanospheres in SiO_2-**6**+ the dispersion remains stable.

The [2]pseudorotaxane recognition-directed templated assembly of binary nanostructures is discussed in the paragraphs that follow.

Previously published data has established the formation of pseudorotaxanes at the surface of metal nanocrystals and their subsequent aggregation.[10,11] These data was supported in both

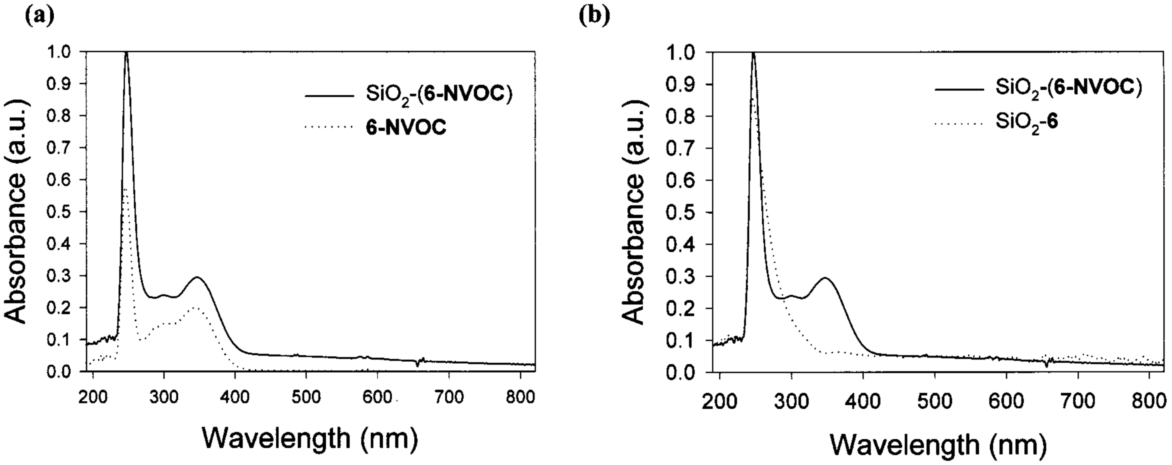


Figure 2. (a) Shown is the UV−vis spectrum obtained for SiO_2-(**6-NVOC**) nanospheres dispersed in chloroform. Also shown is the UV−vis spectrum of **6-NVOC** in chloroform. (b) Shown is the UV−vis spectrum obtained for SiO_2-(**6-NVOC**) dispersed in chloroform before and after irradiation.

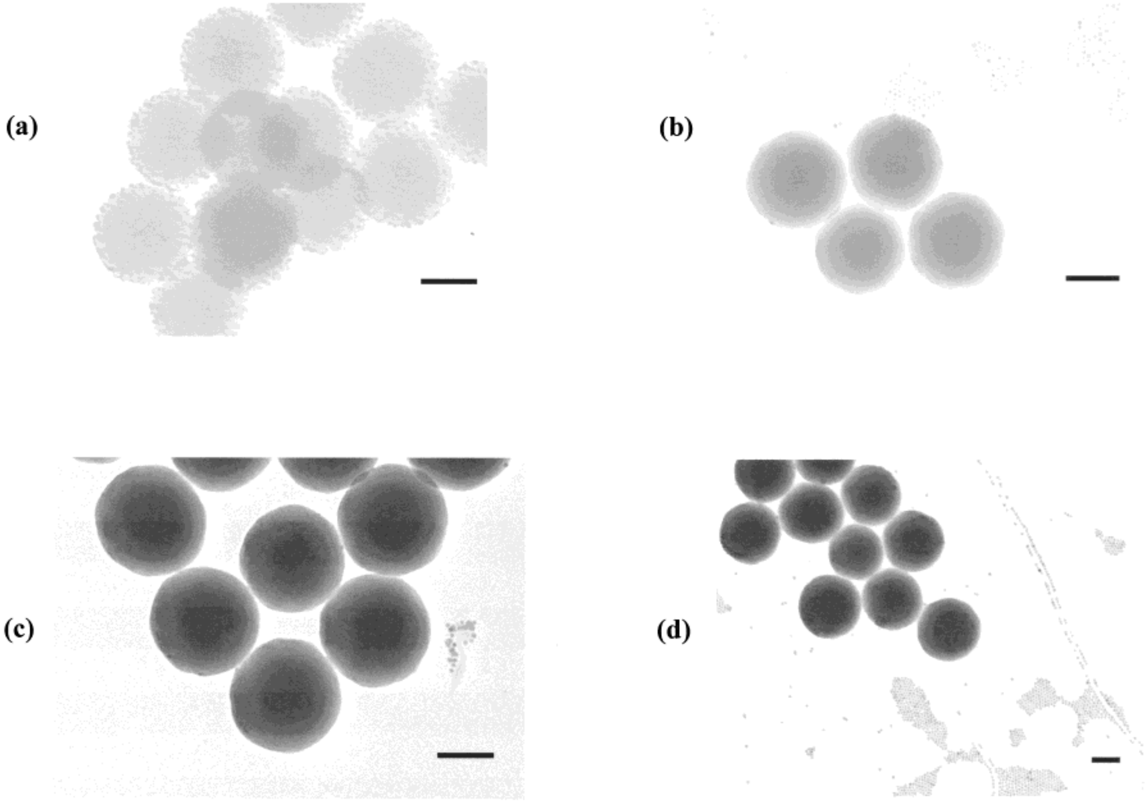


Figure 3. (a) Typical result obtained from mixing a dispersion of Ag-**2** and SiO_2-**6**+. Control experiments involving the addition of silver nanocrystals to silica nanospheres where (b) **2**, (c) **6**+, and (d) both are absent are also included. Scale bar is 100 nm in each case.

cases using high resolution ^1H NMR and, in the latter case, dynamic light scattering. Realizing that high resolution ^1H NMR is not suitable in this case, careful controls have been performed that preclude any alternative to [2]pseudorotaxane formation driving the assembly process and this is further supported by the selective reversal of assembly upon addition of a weak base outlined below.

The addition of Ag-**2**, i.e., silver nanocrystals modified with dibenzo[24]crown-8 recognition motifs, to SiO_2-**6**+ yielded a precipitate within 24 h. This result was not observed in either of the following cases: addition of Ag-**1**, i.e., silver nanocrystals capped with dodecane thiol, to SiO_2-**6**+; addition of Ag-**1** to SiO_2-(**6-NVOC**); addition of Ag-**2** to SiO_2-(**6-NVOC**) over the same time period. Each of these controls represents a situation where either one or both of the recognition elements are absent. A further control was performed: here, dibenzo[24]crown-8, in excess, was added to a chloroformic dispersion of SiO_2-**6**+ and allowed to equilibrate. Further addition of Ag-**2** to this sample did not result in precipitation after a 24 h period. These controls are strong evidence to support our assertion that pseudorotaxane formation is the driving force for the templated assembly of silver nanocrystals on silica nanospheres.

It is evident from TEM analysis (Figure 3) that only when Ag-**2** is mixed with SiO_2-**6**+ is templated nanocrystal assembly observed (Figure 3a). Further addition of Ag-**2** did not improve the density of nanocrystal coverage at the surface of SiO_2-**6**+.

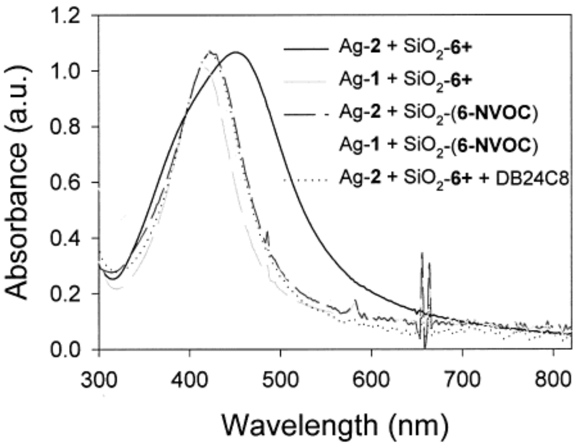


Figure 4. UV−vis spectrum of Ag-**2** and SiO_2-**6**+ obtained 24 h after mixing. Shown also are the spectra obtained for the relevant controls where one or both recognition motifs are absent. Evident from this is the presence of a large absorption band representative of a change in the dielectric environment of silver nanocrystals when these nanocrystals are templated at the surface of silica nanospheres. UV−vis spectra are presented as normalized spectra (uncorrected for scattering).

Furthermore, we can rule out any interaction between silver nanocrystals and silica nanospheres when these materials do not *both* contain **2** or **6**+ chemisorbed on their respective surfaces. For example, in Figure 3b, SiO_2-(**6-NVOC**) is observed on top of a close-packed region of Ag-**2**. The ordering of these nanocrystals is seen to extend beneath the surface of the silica nanospheres without disruption of any nature.

The UV−Visible spectra (Figure 4) further support the TEM data. It is noted that the absorption of **6-NVOC** relative to the surface plasmon resonance of silver nanocrystals is very weak and will not appear in these spectra. In the case where Ag-**2** is added to SiO_2-**6**+, a shift in the surface plasmon band of silver nanocrystals from their solution value, 422 nm, to 452 nm is evident. This red-shift is most likely due to an increase in the effective dielectric environment of the silver nanocrystals.[21,22] In all the remaining control spectra, the surface plasmon band of silver remains at its free solution value. This is indicative of no interaction occurring between silver nanocrystals and silica nanospheres in the absence of *both* **2** and **6**+ chemisorbed at their respective surfaces. Furthermore, no shift in the surface plasmon band is observed for Ag-**2** in the presence of excess dibenzo[24]crown-8 and SiO_2-**6**+. This further confirms our assertion that [2]pseudorotaxane formation is the mechanism for the templated assembly of silver nanocrystals on silica nanospheres. The addition of dibenzo[24]crown-8 has blocked all **6**+ sites on the silica nanospheres and thereby inhibits recognition and binding of Ag-**2** by SiO_2-**6**+.

With knowledge of previous studies on [2]pseudorotaxane formation detailing the dis-assembly of the supramolecular structure,[23] it was proposed that the process of templated assembly of silver nanocrystals on silica nanospheres may be reversed. The addition of triethylamine has been shown to deprotonate dibenzylammonium salts and result in subsequent destruction of any interaction that favors [2]pseudorotaxane formation. An analogous experiment was performed in this study. The TEM data presented in Figure 5a represents an almost complete removal of Ag-**2** from the surface of SiO_2-**6**+ (now SiO_2-**6**), whereas the corresponding UV−vis spectra (Figure 5b) yields the expected blue-shift in the surface plasmon band back to 430 nm. This represents an elegant demonstration of molecular control over the collective optical properties of a composite material and is further evidence that[2]pseudorotaxane formation is driving the templated assembly of binary nanostructures.

One focus of this work is to fabricate useful nanoscale architecture that can be used in potential photonic or electronic applications. To achieve such a goal it is important to demonstrate structural integrity and robustness of material.[24] To this end, we have heated the templated binary nanostructure to investigate how structurally sound the composite material is. Figure 6 shows the results of TEM analysis of thermal processing of the binary nanostructure. It is our belief that, although the silver nanocrystals have altered to form larger crystals, their position at the surface of the silica nanosphere remains intact as is their templated structure. It is noted that the spectroscopic analysis of this material was not performed due to difficulties in obtaining such analysis from a TEM sample. Furthermore, spectroscopic analysis was not performed on isolated samples on a more suitable substrate (e.g., quartz) as this would not allow TEM imaging of the templated assembly. Overall, this indicates a useful metallization process involving initial recognition-directed assembly of binary components followed by thermal processing that *fixes* the structure. Such a result points toward the eventual fabrication of functional

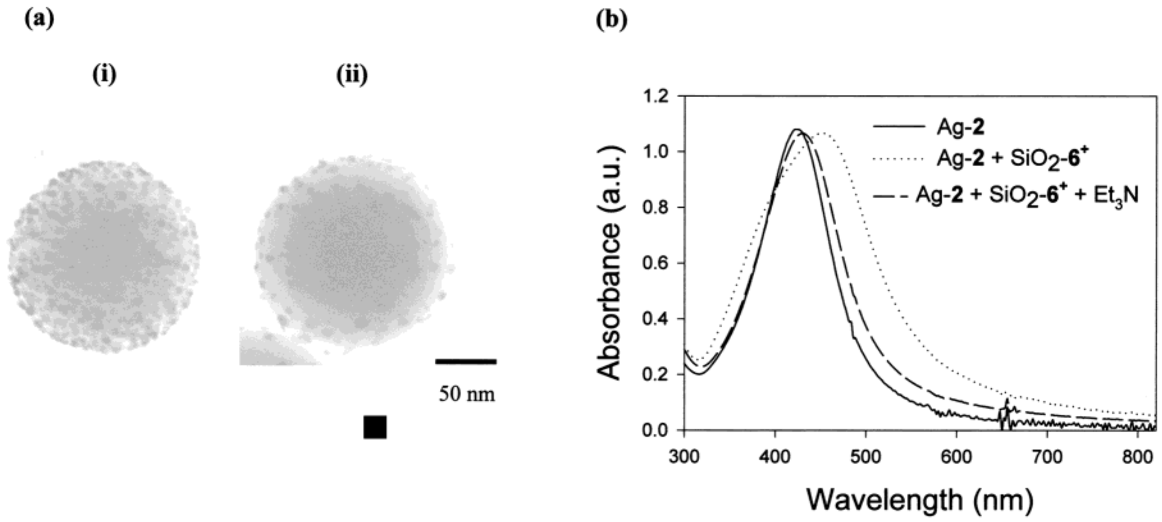


Figure 5. (a) TEM image of a mixture of Ag-**2** and SiO_2-**6**+ (i) before and (ii) after addition of an excess of triethylamine followed by centrifugation. (b) Corresponding UV−vis spectrum showing (i) Ag-**2**, (ii) Ag-**2** on SiO_2-**6**+, and (iii) as for (ii) after addition of triethylamine.

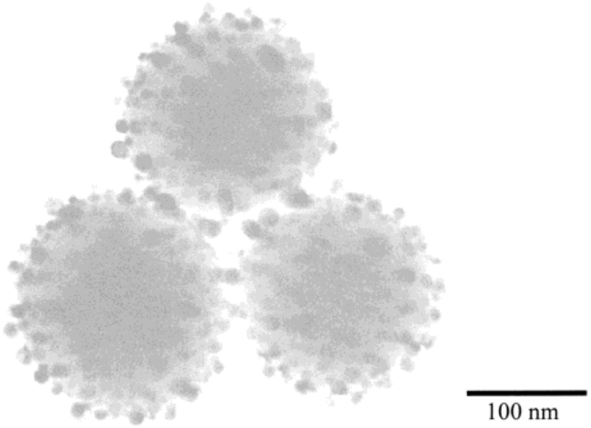


Figure 6. TEM image of templated binary nanostructure after thermal processing. Evident is the presence of larger silver nanocrystals that remain templated at the surface of the silica nanospheres.

nanoscale materials whereby the molecular recognition force that assembles the solid phase materials is eliminated without drastically altering the structural integrity of the resulting assembly.

Conclusion

The recognition-directed templated assembly of a binary nanostructure consisting of dibenzo[24]crown-8-modified silver nanocrystals and dibenzylammonium-modified silica nanospheres has been reported. It has been shown that the dibenzylammonium cation may be generated in situ, at the surface of a silica nanosphere, by photolysis and subsequent protonation of a suitable precursor. It has also been shown that the assembly of this binary nanostructure is due to the formation of a [2]-pseudorotaxane between the interfaces of silver nanocrystals and silica nanospheres. Furthermore, we have demonstrated the ability to reverse the assembly process or, in contrast, the ability to fix the structure into an irreversible state. These results present an insight into the optical properties of a binary nanostructure while also presenting novel control over the structural integrity of the templated assembly.

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