Synthesis, Morphological Control, Dispersion Stabilization and In Situ Self-Assembly of Noble Metal Nanostructures Using Multidentate Resorcinarene Surfactants

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SYNTHESIS, MORPHOLOGICAL CONTROL, DISPERSION STABILIZATION AND

IN SITU SELF-ASSEMBLY OF NOBLE METAL NANOSTRUCTURES USING

MULTIDENTATE RESORCINARENE SURFACTANTS

by

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ABSTRACT

SYNTHESIS, MORPHOLOGICAL CONTROL, DISPERSION STABILIZATION AND IN SITU SELF-ASSEMBLY OF NOBLE METAL NANOSTRUCTURES USING MULTIDENTATE RESORCINARENE SURFACTANTS

Sangbum Han
Old Dominion University, 2016
Director: Dr. Balasubramanian Ramjee

In this dissertation, a detailed investigation on the influence of various macrocyclic resorcinarene surfactants in determining the morphology, stabilization and self-assembly of mono- and bi-metallic nanoparticles was undertaken. Chapter 2 describes the influence of resorcinarene surfactants functionalized with amine- and thiol- headgroups in determining the morphology of monometallic Pt nanoparticles synthesized via the Brust-Schiffrin reaction. We found that while resorcinarene benzylthiol can lead to the formation of highly branched Pt nanostructures, resorcinarene amine can lead to the formation of anisotropic crystalline Pt nanoparticles. Further, we have evaluated the influence of resorcinarene ligands in determining the catalytic activity of these nanoparticles.

Chapter 3 evaluates the role of multidentate resorcinarene surfactants in influencing the morphology and composition of catalytic bimetallic nanoparticles synthesized via a Brust-Schiffrin reduction. We have successfully shown the Pt rich V-shaped PdPt nanoparticles and Pd rich spherical PdPt nanoparticles produced in the presence of resorcinarene amine surfactant. Our detailed mechanistic investigations show newer insights into the formation of anisotropic nanostructures under Brust-Schiffrin reaction conditions. These anisotropic Pt rich bimetallic nanoparticles can act as excellent, stable catalysts for Suzuki cross coupling reactions.

Chapter 4 describes the development of novel multidentate resorcinarene quaternary ammonium salts to stabilize metal nanoparticles in both organic and aqueous medium. We have shown that ionic resorcinarene surfactants can phase-transfer citrate stabilized gold colloids from aqueous dispersions into organic solvents, and their long term dispersion stability depends on the nature of the ionic resorcinarene headgroup. To better understand the interaction of resorcinarene
quaternary ammonium salts, we have also undertaken direct synthesis of gold nanoparticles employing these surfactants and have evaluated their stability under a variety of conditions.

Chapter 5 explores the synthesis of hollow resorcinarene polymeric nanocapsules via thiol-ene photopolymerization using alkene building blocks of various valencies. We have shown that the thickness and rigidity of hollow polymeric nanocapsules can be varied systematically by altering the valencies of the alkene building blocks. We have employed hollow, polymeric, thiol-ene resorcinarene nanocapsules as 3-D template reaction vessels for the in situ synthesis and assembly of platinum nanoparticle aggregates and have shown their utility as hydrogenation catalysts.
This dissertation is dedicated to the Lord my God and the following people:

- **My parents**: Heung Soo Han and Sook Ja Kang.
- **My sister and her family**: Soyoung Han, Guan-Hong Lee and Hawa Lee.
- **My brother and his family**: Sang-Min Han, Hyoung-Ah Baek, Chaehee (Cherry) Han and Becky Han.
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For whoever exalts himself will be humbled, and whoever humbles himself will be exalted.

- Matthew 23:12 -

’Call to me and I will answer you and tell you great and unsearchable things you do not know.’

- Jeremiah 33:3 -

For I know the plans I have for you,” declares the LORD, ”plans to prosper you and not to harm you, plans to give you hope and a future.

- Jeremiah 29:11 -

I would like to first give thanks to the Heavenly Father. The Lord has given me strength, confidence, and wisdom so that I could successfully carry out the tasks He laid before me. Throughout this Ph.D. journey, the Lord has taught me how to be humble so that He can exalt me for His glory. When I was full of fear, He said to me, ”Do not fear.” He was always with me. I confess that it was all God who has brought me this far and the reason I was able to stay strong.

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CHAPTER 1
INTRODUCTION

1. Nanoparticles

Nanoparticles have at least one or more dimensions, i.e., length, width or thickness under 100 nm.\(^1\)\(^{-3}\) Fundamental studies and applications using nanoparticles have emerged as one of the most important fields in modern science.\(^2\) Compared to bulk materials, nanoparticles exhibit size\(^4\) and shape\(^5,6\) dependent optical,\(^7,8\) electrical,\(^9,10\) and catalytic\(^3,6,11\) properties. The decrease in the size of the nanoparticles can: (1) change their electronic structure,\(^12\) and (2) expose more of the high-energy surface atoms on the surface of the nanoparticles.\(^13,14\) These properties have been exploited for applications in optoelectronics,\(^15,16\) sensing,\(^17\) imaging,\(^18\) catalysis\(^14,19\) and biomedicine.\(^20\)

Nanoparticles have a strong tendency to aggregate due to attractive van der Waals forces, which often leads to the loss of their unique properties.\(^21\)\(^{-23}\) To prevent their aggregation, a number of stabilizers such as surfactants,\(^19,24-26\) polymers,\(^19,27,28\) and dendrimers\(^24,29-31\) have been developed. Macromolecules such as polymers or oligomers and dendrimers can be absorbed on the surfaces of the particles to provide steric stabilization.\(^22,29-32\) They generate a protective steric layer around the nanoparticle and prevent their agglomeration. Ligand passivation\(^21,22\) is a sub-set of steric stabilization and is based on the coordination of ligands such as phosphines,\(^33,34\) thiols,\(^35,36\) or amines\(^37-39\) to metal nanoparticles. Ionic compounds such as sodium citrate can provide an electrical double-layer around the particles in solution, which results in electrostatic stabilization.\(^22\)

Fabrication methods for metal nanoparticles can be classified as "top-down" or "bottom-up" approaches.\(^40,41\) "Top-down methods" are based on the mechanical grinding of bulk metals to obtain nano-sized ultrafine particles.\(^40,41\) "Bottom-up" approaches generally result in a more precise control of morphology than "top-down" approaches.\(^22\) Typically, the "bottom-up" method proceeds in the following manner. The reduction of metal ions leads to the formation of nuclei, which grow to form metal nanoparticles.\(^22\) Representative "bottom-up" approaches include one-
or two-phase chemical, sonochemical, electrochemical, photochemical, and radiolytic reductions.

2. Morphology of nanoparticles

Several synthetic approaches currently employed for the preparation of nanoparticles such as two-phase reactions, citrate reduction, and inverse micelle templated synthesis typically lead to the formation of spherical or pseudospherical nanoparticles. In general, nanoparticles with inherent high surface to volume ratio have high surface energy due to excess free energy per unit area. The formation of spherical nanoparticles is not surprising, as most particles tend to form low-index crystal planes in order to minimize their surface energy (or tension). The size of such nominally spherical nanoparticles can be controlled by altering kinetic and thermodynamic conditions such as concentrations of the starting materials, time, temperature and others. Further, post synthetic methods have also been employed to alter the size of the nanoparticles. For example, Prasad and Sahu reported the effect of time and temperature in determining the size of spherical Au nanoparticles during digestive ripening reaction. AuCl₃ was dissolved in 4-tert butyltoluene and reduced by NaBH₄ in water in the presence of didodecyl dimethylammonium bromide, leading to the formation of polydisperse spherical nanoparticles. Hexadecanethiol (HDT) was added to this colloidal solution to obtain HDT capped Au nanoparticles 6.3 ± 2.2 nm in size. The colloidal dispersions were heated at different temperatures (60, 90, 120, 150, and 180 °C) for various time periods (1, 3, 9 and 24 h). While the size of the nanoparticle remained constant at relatively lower temperatures (60 and 90 °C), the dimensions of the nanoparticles increased at higher temperatures. For example, the particle size increased from 7 ± 0.7 nm to 10.8 ± 1.5 nm at 120 °C.

Size of the nanoparticle influences its optical and electronic properties. In particular, as the size of the noble metal (Au or Ag) nanoparticle changes, the observed color changes. In the case of Au nanoparticles, Wang and coworkers observed that the surface plasmon resonance of the Au nanoparticles changed from 525 to 1150 nm as their size increased from 15 to 190 nm. This phenomenon is due to the collective oscillation of the electrons in the conduction band, which is known as surface plasmon resonance. The intrinsic characteristics of the surface plasmon resonance (SPR) was first rationalized by Mie in 1908. When the physical size of the metal
nanoparticle decreases, the electron is more confined leading to a large band gap energy between the conduction and valence bands. This causes a blue-shift in the optical absorption maximum. The optical properties of the metal nanoparticles can be altered by changing their size and this offers numerous advantages for applications in sensing, diagnostics, photothermal therapeutics and many other areas.

Figure 1. Typical structure of (a) (111) and (b) (100) facets.

At a microscopic level, spherical nanoparticles are made up of a number of 100 and 111 surface planes (Figure 1) with smooth corners and edges. The type of exposed crystalline facets can be controlled by the shape of the nanoparticles. In order to control the nanoparticle's surface structure, one approach is to introduce surface directing agents during nanoparticle synthesis. These stabilizing agents can limit the growth of nanoparticles in particular directions by getting adsorbed on select surfaces of the nanoparticles. In the case of Pt group metal nanoparticles, bromide ions and hydrogen can control the shape of the nanoparticles. For example, NaBH₄
reduction of $\text{H}_2\text{PtCl}_6$ aqueous solution in the presence of tetradecyltrimethylammonium bromide (TTABr) can produce Pt cubes with (100) surfaces. TTABr plays a dual role in this synthesis as both a surface directing agent and a surfactant (Figure 2).\textsuperscript{66,69} Lee and coworkers have also prepared Pt nanoparticles with various shapes such as cubic, cuboctahedral, and porous structures in the presence of TTABr.\textsuperscript{66} These shapes were controlled by adjusting the pH value using reducing agents. With a high concentration of $\text{NaBH}_4$, the pH increases leading to a lower reduction rate. This enables selective growth on the (100) facets to form into cubic Pt nanoparticles. In addition, $\text{Br}^-$ is known to selectively adsorb onto (100) facets and stabilize them, resulting in the formation of (100)-terminated cubic metal nanocrystals.\textsuperscript{70} On the other hand, the adsorption of poly vinylpyrrolidone (PVP) favors the formation of (111) faces. $\text{H}_2$ reduction of $\text{H}_2\text{PtCl}_6$ in the presence of PVP results in Pt tetrahedral shapes with (111) surfaces.\textsuperscript{67}
Figure 2. TEM images (scale bar = 50 nm) of (a) cuboctahedral, (c) cubes, and (e) porous particles. HRTEM images (scale bar = 3 nm) of (b) a cuboctahedron along the (111) facets, (d) a cube along the (100) facets, and (f) a porous particle. Reproduced with permission from ref. 58a.

Typically crystals grow rapidly in a perpendicular direction to a high-index facet with high energy. Thus, the high-index facets are eliminated to reduce the high surface energy during the formation of nanoparticles. Thus, the formation of high-index planes is usually not easy. Wang and coworkers reported an electrochemical method for the synthesis of tetrahedrahedral Pt
nanocrystals. In this approach, large Pt spherical nanoparticles (750 nm in size) were electrodeposited on a Glassy carbon substrate. Under a square-wave potential, the large Pt nanoparticles were electrochemically transformed into tiny Pt crystallites and subsequently these Pt crystallites grew into tetrahedral shaped Pt nanocrystals (217 ± 23 nm). Other high index structures such as concave hexoctahedral nanocrystals with (321) facets, trapezoohedral nanocrystals with (311) facets and multiple twinned nanorods with (321), (210), (730), (520), (310) and (410) facets have also been prepared by electrochemical approaches. In spite of recent advances, the techniques and approaches for shape control are currently underdeveloped in comparison to size-control techniques.

3. Nanocatalysis

Nanocatalysis, i.e., catalysis mediated by nanoparticles, serves as a bridge between the well-established disciplines of homogenous and heterogeneous catalysis. Its appealing feature is the ability to correlate catalytic activity, stability, and selectivity with tunable physical characteristics of the nanoparticle such as size, surface composition, support, and shape. In recent years, examples of nanocatalysis have exponentially increased and unveiled recoverable and recyclable catalysts with distinct catalytic activity in a variety of reactions including oxidation, hydrogenation, electron transfer, cross-coupling, and fuel cell reactions, amongst others. Furthermore, metal nanoparticles also have shown unique catalytic properties. For example, Tamura and Fujihara have found that chiral palladium nanoparticles can catalyze the hydrosilylation of styrene with trichlorosilane at room temperature, while palladium complexes coordinated with a bisphosphine ligand cannot catalyze the hydrosilylation reaction even at 80 °C.

Nanocatalysis reactions rely on the surface of nanocatalysts and metallic nanocatalysts having sharp edges, sharp corners, or rough surfaces, which are more active. Catalytic performance of nanoparticles is dependent on the exposed surface area of the nanoparticles and their surface properties. The distinct surface atomic arrangements resulting from different shapes of nanoparticles can also influence the selectivity and reactivity in structure sensitive reactions. For example, the hexagonal Pt (111) crystal surface is more active than the cubic Pt (100) surface in the dehydrocyclization of n-heptane. On the other hand, the cubic Pt (100)
surface is more active than the hexagonal Pt (111) surface for the isomerization of isobutene.\textsuperscript{80} El-Sayed and coworkers have evaluated tetrahedral, cubic, and spherical Pt nanoparticles as catalysts in the electron transfer reaction of hexacyanoferrate(III) and thiosulfate ions yielding hexacyanoferrate(II) and tetrathionate ions.\textsuperscript{81} They found that tetrahedral Pt nanoparticles with the highest fraction of surface atoms on the edges and corners demonstrated the highest catalytic activity with the lowest activation energy.\textsuperscript{81} El-Sayed and Narayanan have shown that the catalytic activity of Pt nanoparticles in the Suzuki reaction (equation 1) can be improved by changing the shape of the Pt nanoparticles.\textsuperscript{14} While spherical Pt nanoparticles are ineffective in catalyzing the Suzuki coupling reaction,\textsuperscript{82} they showed that tetrahedral Pt nanoparticles can catalyze the Suzuki reactions albeit with a modest 14 ± 5 % yields.\textsuperscript{14} Unfortunately, these tetrahedral Pt nanoparticles have poor catalytic recyclability. The shape of the Pt nanoparticles changes during catalysis reactions such as the Suzuki coupling\textsuperscript{14} and electron-transfer.\textsuperscript{13} During the course of the catalysis, they observed that the atoms located on the corners and edges of the nanoparticles moved and rearranged, leading to the formation of more stable nanoparticles with near spherical shapes, along with larger sized nanoparticles formed via the Ostwald ripening process. In another report, their group showed that in the Suzuki coupling reactions, nearly spherical Pd nanoparticles stabilized by PVP\textsuperscript{83} were generated upon recycling the nanoparticle catalysts, and their catalytic activity decreased with the number of catalytic cycles. They attributed this factor to the fact that the spherical nanoparticles have less sharp edges and corners with higher activation energies.\textsuperscript{81}

\[
\begin{align*}
\text{X} & \quad \text{OH} \\
+ & \quad \text{OH} \\
\text{Pt nanocatalysts} & \quad \text{Base} \\
\end{align*}
\]

\[X = \text{Cl, Br, I}\]

Single-crystal surfaces of bulk Pt metal having high-index planes have shown higher catalytic activity than other stable surface planes such as (100), (111), and (110).\textsuperscript{66} The tetrahexahedral Pt nanocrystals (Figure 3) bounded by high-index facets (730), (210) and (310) were greatly effective as catalysts in the electrooxidation of formic acid (equation 2) and ethanol (equation 3).\textsuperscript{71} The current density of formic acid oxidation on the tetrahexahedral Pt nanocrystals is
almost 2-fold higher than that on Pt nanospheres (up to 400 %) or commercial Pt/C (up to 310 %). For ethanol oxidation, the current density on the tetrahedral Pt was much higher than that on Pt nanospheres (up to 230 %) or commercial Pt/C (up to 330 %).

Figure 3. TEM images of tetrahedral Pt nanocrystals bound by high-index facets (730), (210) and (310). Reproduced with permission from ref. 61.
HCOOH $\rightarrow$ CO $\rightarrow$ CO$_2$ + 2H$^+$ + 2e$^-$ \hspace{1cm} (2)

CH$_3$CH$_2$OH $\rightarrow$ CO$_2$ + H$_2$O \hspace{1cm} (3)

Xia and coworkers have evaluated crystal facet-dependent chemical catalysis using concave Pd nanocubes with (730) facets and conventional Pd nanocubes with (100) facets.$^{84}$ In the Suzuki coupling reaction, the concave Pd nanocubes with (730) facets yielded 99% of biphenyl in 20 min, whereas the conventional Pd nanocube with (100) facets yielded 38% of biphenyl in the same time frame.$^{84}$ His research group has reported a method to control the morphology of PdPt nanostructures to improve their catalytic properties.$^{85}$

Pt is known to be the most effective catalyst for both hydrogen oxidation and oxygen reduction (equation 4 and 5), in a proton-exchange membrane (PEM) fuel cell.$^{86}$ The oxygen reduction reaction (ORR) activity is strongly dependent on the surface area and specific active facets of Pt catalysts.$^{87}$ Due to the difficulty of synthesizing such catalysts, commercial Pt/C has been commonly used in the ORR.$^{88}$ In order to enhance the electrocatalytic performance of Pt catalysts, Xia et al. synthesized PdPt nanodendrites consisting of Pt branches on Pd nanocrystals with a mix of (111) and (100) facets (Figure 1a and 1b) in an aqueous solution.$^{85}$ The ORR was carried out in O$_2$ saturated 0.1 M HClO$_4$ solutions using a glassy carbon rotating disk electrode at room temperature. The PdPt nanodendrites showed 2.5 time higher activity than commercial Pt/C and 5 times higher activity than the 1st generation Pt black catalyst. Sun and coworkers have evaluated the catalytic activity of (730)-faceted tetrahexahedral (THH) Pd nanocrystals in electrooxidation of ethanol in alkaline media.$^{89}$ The THH Pd nanocrystals enclosed by (730) high-index facets exhibited 4 - 6 times higher catalytic performance than commercial Pd black catalyst.$^{89}$

Anode: O$^{2-}$ + H$_2$ $\rightarrow$ H$_2$O + 2e$^-$ or H$_2$ $\rightarrow$ 2H$^+$ + 2e$^-$ \hspace{1cm} (4)

Cathode: 1/2O$_2$ + 2e$^-$ $\rightarrow$ O$^{2-}$ or 1/2O$_2$ + 2H$^+$ + 2e$^-$ $\rightarrow$ H$_2$O \hspace{1cm} (5)

Notwithstanding many advantages of nanoparticle catalysts, the current challenges include: (1) reshaping$^{14}$ and (2) aggregation of the nanoparticles$^{13,90}$ and (3) limited recyclability with decreased catalytic activity upon recycling.$^{14}$ Hence, despite the recent advances, there is a need
to improve the catalytic activity of the nanoparticles without compromising on their long-term stability and recyclability.

4. Brust-Schiffrin Nanoparticle Synthesis

Brust-Schiffrin two-phase synthesis has been and is currently the most-commonly used method for the synthesis of metal nanoparticles.\textsuperscript{10,43,91} It is a versatile and simple approach. In the original synthesis, HAuCl\textsubscript{4} is phase-transferred from an aqueous to an organic phase (i.e., toluene) with the aid of tetraoctylammonium bromide, a phase transfer agent (equation 6); and subsequently the metal salt in the organic phase is reduced by the addition of a thiol and aqueous sodium borohydride (equation 7), leading to the formation of thiolate stabilized gold nanoparticles.

\[
\text{[AuCl}_4^-\text{]}_{\text{water}} + [(\text{C}_8\text{H}_{17})_4\text{N}^+\text{Br}^-]_{\text{Toluene}} \rightarrow [(\text{C}_8\text{H}_{17})_4\text{N}^+\text{AuCl}_4^-]_{\text{Toluene}} \quad (6)
\]

\[
[(\text{C}_8\text{H}_{17})_4\text{N}^+\text{AuCl}_4^-]_{\text{Toluene}} + [\text{RSH}]_{\text{Toluene}} \xrightarrow{[\text{BH}_4^-]_{\text{water}}} [(\text{Au})_x(\text{SR})_y]_{\text{Toluene}} \quad (7)
\]

Typically, in Brust-Schiffrin synthesis, thiols are most commonly used as stabilizers\textsuperscript{10} as they offer robust steric stabilization of metal nanoparticles due to strong binding to the metal surfaces.\textsuperscript{23} This method typically leads to synthesis of nanoparticles with dimensions up to 5.2 nm. Murray and coworkers have shown that the dimensions of the nanoparticles can be varied by varying the equivalents of thiol added and the temperature of the Brust-Schiffrin reaction.\textsuperscript{92} Though initially developed for gold nanoparticles subsequently it has been applied to other mono\textsuperscript{93} and bimetallic nanoparticles.\textsuperscript{94,95}

From a mechanistic point of view, initially it was assumed that the addition of the thiol led to the formation of [AuSR]\textsubscript{n}-like polymers after the reduction of Au(III) to Au(I) by the alkanethiol.\textsuperscript{91} In 2010, Lennox and Goulet demonstrated that tetraalkylammonium metal complexes are formed before the addition of the reductant in the two-phase reactions and polymeric metal-thiolates are formed in the one-phase reactions.\textsuperscript{96} Subsequently Tong and coworkers suggested the presence of an inverse micelle formed by tetraoctylammonium bromide (TOABr), where the metal nucleation occurred and nanoparticles were generated.\textsuperscript{97} The formation of metal to chalcogen bonds occurred after the synthesis of the nanoparticles and occurred outside the inverse micelle
They also highlighted the role of water in the Brust-Schiffrin nanoparticle synthesis, and found that the presence of water and the amount of water are important in the formation of the nanoparticles. Remarkably, Au nanoparticles obtained in the presence of more water had a much smaller size with a narrower size distribution. Recently, Zhu et al. monitored 1-octadecanethiol and Au^{3+} solution by NMR spectroscopy. They showed that tetraalkylammonium gold complexes ([TOA][AuX_2]) and soluble gold thiolate species ([TOA][AuSRX] and [TOA][Au(SR)_2]) can be formed depending on the reactant concentration prior to the addition of the reducing agent. The intermediate precursors containing ([TOA][AuX_2]) and excess thiol were reduced to monodispersed small Au nanoparticles, whereas the precursors containing mainly soluble gold thiolate species ([TOA][AuSRX] and [TOA][Au(SR)_2]) led to polydispersity and partial aggregation of the nanoparticles. Kumar and coworkers have recently questioned the presence of the inverse micelle nanoreactor. Despite the recent advances, the complete mechanistic details of the Brust-Schiffrin reaction are still unclear.

5. Ligand effects

In general, metal nanoparticles can be prepared in the presence of linear surfactants which can form self-assembled monolayers (SAMs) on the metal surface. Such surfactants can stabilize the nanoparticles and prevent them from agglomerating. Beyond thiol based surfactants, a variety of surface functional groups such as amines, phosphines and silanes have been effectively used in the stabilization of metal nanoparticles. The ligands employed in the nanoparticle syntheses can play a role in (i) improving the kinetic and thermodynamic stability of the precursors, (ii) stabilizing colloids, (iii) determining the growth of nanocrystals, and as (iv) reducing agents and (v) oxidative etchants. In addition capping ligands also influence the solubility of nanoparticles.

The mobility of the ligands also plays a crucial role in the dispersion stability of the nanoparticles. Both the Lennox and Murray groups proposed that the ligands on the nanoparticle's surface can be mobile and reach self-optimized binding sites. Rotello and coworkers employed multivalent flavin binding sites to investigate the rate of surface diffusion of the ligands on functionalized gold nanoparticles. They concluded that the diffusion rate was
very slow at room temperature. On the other hand, Werts group observed a rather rapid lateral diffusion on alkyl disulfide protected Au nanoclusters using fluorescence titration. The mobility of thiols in the SAM can provide environmentally responsive systems. Such materials can be used in a wide range of applications from biological probes to novel catalytic materials. In contrast to these reports, Chechik and coworkers observed no mobility of thiolate ligands on the Au nanoparticle’s surface at room temperature, and further only some minimal redistribution of the ligands occurred even at high temperature (90 °C).

Pileni and coworkers have shown that the length of the stabilizing ligand has an effect on the final size of the nanocrystals synthesized. Pt nanoparticles were prepared by the Brust-Schiffrin method in the presence of various alkylamines with different length of alkyl chains, ranging from hexylamine to octadecylamine (C_{6}H_{13}NH_{2}, C_{7}H_{15}NH_{2}, C_{8}H_{17}NH_{2}, C_{9}H_{19}NH_{2}, C_{10}H_{21}NH_{2}, C_{12}H_{25}NH_{2}, and C_{18}H_{37}NH_{2}). The results indicated an inverse relationship between the length of the alkylamine and the size of near spherical Pt nanoparticles. The Pt nanoparticle diameter decreases (2.60 nm to ~ 1.60 nm) as the length of the alkylamine increases. They suggested that this result may be attributed to their different solubility in toluene. An alkylamine with a long hydrocarbon chain is much less soluble in toluene, which results in the formation of compact palisade layers on the surface of the Pt nanoparticles. These compact palisade layers formed with the long chain alkylamine, inhibits the growing Pt particle.

Ramirez et al. have studied the effect of organic ligands (hexadecylamine and polyphosphines), their concentration, and reaction media (THF and toluene) on the morphology of Pd nanoparticles. In the presence of polyphosphines, spherical Pd nanoparticles with ~2 nm size and good stability could be prepared. In the case of hexadecylamine as a stabilizer, the morphology of the Pd nanoparticles was dependent on the concentration of ligands and organic solvents. In the presence of 0.1 equivalent of hexadecylamine, agglomerated Pd nanoparticles were obtained in THF or toluene. When using 1 equivalent of hexadecylamine, the nanoparticles were somewhat elongated in shape and were also less aggregated. In the presence of 10 equivalent of hexadecylamine in THF, the particles showed good stabilization and a near spherical shape with an average size of 6 nm. They suggested that THF also participates in the stabilization of Pd nanoparticles. However, the nanoparticle in toluene still showed elongated structures when using 10 equivalent of hexadecylamine. These results showed that the size and
shape of nanoparticles can be controlled by the nature of coordinating ligands and the reaction medium. Furthermore, a strongly coordinating ligand such as polyphosphine contributes to the formation of small sized spherical Pd nanoparticles without any agglomeration.

Mariscal and coworkers carried out an atomistic simulation study on the effect of ligands in determining the morphology and crystalline structure of Au nanoparticles.\textsuperscript{113} In the presence of alkyl thiolates (−SR), a strong passivating agent, nanoparticles were strongly deformed, while in the presence of alkyl amines (−NH\textsubscript{2}R), a soft passivating agent, there was no influence on the shape and crystallinity of the nanoparticles.

Further ligands can also impact the catalytic ability of nanoparticles. Despite their utility, thiols are known to poison catalytic metal nanoparticles due to their strong interaction with the surface of nanoparticles.\textsuperscript{114,115} For this reason, catalytic nanoparticles are often protected by weak binding surfactants such as anions, amine surfactants, etc.\textsuperscript{21}

Korgel and Stowell carried out the synthesis of iridium (Ir) nanocrystals in the presence of four different capping ligands: oleic acid/oleylamine, trioctylphosphine (TOP), tetraoctylammonium bromide (TOABr), and tetraoctylphosphonium bromide (TOPBr).\textsuperscript{23} The oleic acid/oleylamine yielded high-quality crystalline Ir nanocrystals with a narrow size (1.5 to 5 nm) and shape distribution. The TOP stabilized particles were extremely polydisperse (10 to 100 nm) and contained irregular shapes. The TOABr stabilized Ir nanocrystals were crystalline and relatively monodisperse (1.5 to 3 nm). The TOPBr stabilized Ir nanocrystals were crystalline but slightly larger in size (2 to 5 nm) and were polydisperse. They have also demonstrated that the capping ligand significantly affects the catalytic activity of these nanocrystals.\textsuperscript{23} They reported an inverse relationship between stability and the catalytic ability of the nanoparticles.\textsuperscript{23} They found that as the interaction between the stabilizer and the metal surface increases leading to better stabilization of the nanoparticles, the catalytic activity decreases.\textsuperscript{21,23}

Somorjai and coworkers compared the catalytic activity of Pt nanoparticles stabilized with four different surfactants such as thiol, amine, tetraalkylammonium bromide, and a polymer.\textsuperscript{116} During CO oxidation (equation 8), tetraalkylammonium bromide stabilized Pt nanoparticles exhibited higher catalytic activity presumably due to the weak binding between surfactant and Pt metal. These results are consistent with the observations of Korgel and coworkers.\textsuperscript{23}
In order to evaluate the role of ligand concentration on the catalytic behavior of Ru nanoparticles, Salas and coworkers carried out catalytic hydrogenation of 1,3-cyclohexadiene using 1-octylamine (OA) stabilized Ru nanoparticles with different ratios of OA ligand/Ru such as Ru_{OA0.2}, Ru_{OA0.5}, and Ru_{OA1} and ligand-free Ru nanoparticles.\textsuperscript{117} The catalytic activity decreased as the ratio of the ligand/Ru increased from 0.2 to 1. It can be attributed to steric hindrance resulting in the decreased probability for the reactants to interact with the surface of the nanoparticles.

6. Nanoparticle synthesis with polymer ligands

Polymer-nanoparticle nanocomposites obtained by the integration of polymers and nanoparticles, combine the desirable properties of nanoparticles and polymers towards applications in wide ranging areas from electronic devices\textsuperscript{118} to catalysis.\textsuperscript{119} These diverse\textsuperscript{120-122} nanocomposites can be widely used as versatile functional materials as they exhibit advantageous electrical, optical or mechanical properties.\textsuperscript{120,122}

Polymers\textsuperscript{123} and dendritic architectures\textsuperscript{124} have been effectively used as templates to control the size,\textsuperscript{125} size distribution\textsuperscript{126} and shape\textsuperscript{127} of nanoparticles and for the stabilization of nanoparticles.\textsuperscript{128-131} Nie and Kairdolf showed the enhanced stability of Au nanoparticles passivated by multidentate polymer ligands.\textsuperscript{131} These polymer ligands contain \textasciitilde14 carboxylic functional groups in each molecule, which can bind to the surface of the nanoparticles via electrostatic interactions.\textsuperscript{131} In contrast to traditional monovalent ligands, the formation of nanoparticles in the presence of multidentate polymer ligands occurs via a different nucleation and growth mechanism.\textsuperscript{92,95} These multidentate ligands bind strongly to the surface of the nanoparticles during the nucleation-growth process resulting in monodisperse\textsuperscript{131} and highly stable colloids.\textsuperscript{129} In the conventional citrate reduction, the synthesis of Au nanoparticles proceeds through a transient intermediate step (optically red-shifted) and subsequently progresses to form Au nanoparticles.\textsuperscript{132} In contrast, in the presence of multidentate polymers the transient stage is absent.\textsuperscript{131} The multidentate polymer ligands give rise to a slower nanoparticle-growth rate and reduced Ostwald ripening due to the increased binding affinity\textsuperscript{130} and steric
hindrance.\textsuperscript{128,129} Decreased growth rate potentially leads to better control of the nanoparticle size.\textsuperscript{131}

Dendrimers, another suitable class of polymers, have a central core with extended hyperbranched architecture (Figure 4).\textsuperscript{133,134} The dendrimers have been acting as hosts for guest molecules\textsuperscript{135,136} and used as potential templates for the formation of organic-inorganic nanocomposites.\textsuperscript{31,124,137,138} The use of dendrimers offers the following advantages: (1) preparing monodisperse noble metal nanoparticles,\textsuperscript{29,133} (2) providing superior stabilization of nanoparticles during any catalysis reaction,\textsuperscript{139} and (3) immobilization on electrode surfaces.\textsuperscript{140} Based on these advantages, Crooks and Zhao have shown the enhanced electrocatalytic activity of dendrimer/Pt nanocomposites in the ORR.\textsuperscript{140} As dendrimers take on globular morphologies, with a sufficient number of branching generations, they become monodispersed in size and feature steric overcrowding at the periphery with an almost hollow core.\textsuperscript{133} Functionality can be accurately assigned at the periphery or along the branching chains of these dendrimers.\textsuperscript{133} Blending functionality and size monodispersity allows this class of polymers to be unique macromolecular components to be utilized in assembling nanoparticles and regulating interparticle distances.\textsuperscript{133,141}
Kakkar and coworkers have shown the shape control of silver nanoparticles in the presence of OH terminated dendrimers. They showed that as the number of branches of the dendrimers increases, the shape of the silver nanoparticles evolves from spheres to cubes. These dendrimers contain phenolic hydroxyl groups which act as reactive and capping sites, allowing for chemisorption of silver ions (Ag\(^+\)) onto the peripheral hydroxide groups during synthesis. Therefore, the formation of the nanoparticle occurs on the exterior of the dendrimers and spherical nanostructures are dominantly formed. As the number of dendrimer branches increases, an internal cavity forms and the growth of the silver particles takes place in the interior of the dendrimer leading to the formation of cubic structures.
7. Polymers as templates in assembling nanoparticles

Polymer scaffolds can also act as functional elements and aid in the assembly of nanoparticles into one-dimensional (1-D) nanocomposites,\textsuperscript{141} well-ordered 2-D arrays\textsuperscript{142} or complex 3-D aggregates.\textsuperscript{143} Highly organized 1-D, 2-D, and 3-D nanocomposites exhibit unique magnetic, optical and electronic properties based on interparticle spacing\textsuperscript{144} and their dimensions.\textsuperscript{145}

There have been some reports in the literature that polymer morphologies can lead to assembling nanoparticles in organized 1-D and 2-D networks.\textsuperscript{121,146,147} Particularly, the architecture of block copolymers (polymers that consist of two or more long sequences of distinct co-monomers) is very useful as a template for selective incorporation or patterning of nanoparticles.\textsuperscript{148} Zubarev and coworkers have shown that 1-D tubular nanoparticle arrays are formed using a micelle-like aggregation of polystyrene-b-poly(ethylene oxide) (PS\textsubscript{40}-PEO\textsubscript{50}) which contains a carboxylic acid group (Figure 5).\textsuperscript{146} In order to induce a cylindrical aggregation, block copolymer with PS and PEO blocks was prepared, mixed with pre-made 2 nm Au nanoparticles functionalized with mercaptophenol in a mixture of water and THF solution and dialyzed against DI water. Consequently, well-defined 1-D tubular nanoarrays of Au-(PS\textsubscript{40}-PEO\textsubscript{50})\textsubscript{n} nanoparticles with 18 ± 2 nm in diameter and ~100 nm in length were assembled.
Thomas and coworkers have shown the 2-D patterning of nanoparticles using the lamellar morphology of block copolymers.\textsuperscript{147} To obtain the 2-D block copolymer/nanocrystal films, a high molecular weight poly(styrene-b-ethylene propylene) (PS-PEP) (4 × 10\textsuperscript{5} g/mol) and two different-sized nanoparticles, 1-octadecanethiolate stabilized Au nanoparticles (3.5 ± 1 nm) and hexamethylenedisilazane coated silica nanoparticles (21.5 ± 2.5 nm), were mixed in toluene and annealed at 60 °C for 3 days. This resulted in autonomous particle separation and the 2-D formation of organized stack-like structures of silica and Au nanoparticles. Au nanoparticles were located along the intermaterial dividing surface between the PS and PEP domains, and silica nanoparticles were found to be in the PEP domains. They suggested the importance of

Figure 5. Schematic representation (A) and TEM (B) of amphiphilicity-driven self assembly of Au-(PS-PEO)_n NPs.\textsuperscript{146} Reproduced with permission from ref. 124a.
entropic contributions in the formation of these structures. The template assembly of nanostructures on curved 3-D substrates is nascent when compared to the assembly of nanostructures on macroscopic flat surfaces.\textsuperscript{149}

One of the major challenges in the fabrication of polymer nanoparticle composites is the effective dispersion of nanoparticles within the polymer hosts,\textsuperscript{120} which often requires modification of one of the components.\textsuperscript{121} Hence, there is a need to develop morphologically distinct, chemically compatible, polymer templates for nanoparticle synthesis and assembly.

8. **Macro cyclic ligand stabilized nanoparticles**

Macro cyclic surfactants are versatile building blocks in supramolecular chemistry.\textsuperscript{150} In particular, cyclodextrins, calixarenes, cucurbiturils, and recently pillararenes are well-studied supramolecular macrocycles (Figure 6). There is currently an interest in the integration of these macro cyclic supramolecules and nanoparticles. In nanoparticle synthesis, these macro cyclic molecules can act as a reducing agent, stabilizer and further as a surface-modifier (post synthesis).\textsuperscript{150} Furthermore, the use of multidentate macro cyclic ligands to passivate nanoparticles is an attractive strategy to provide enhanced catalytic activity without compromising on the nanoparticle stability.\textsuperscript{131,151,152} The incomplete packing of large macro cyclic surfactants on nanoparticle surfaces leads to accessible surface area for catalysis.\textsuperscript{153,154}
Luong and coworkers have reported the synthesis of spherical gold nanoparticles by the reduction of HAuCl₄ with either sodium borohydride or sodium citrate in the presence of α-, β-, and γ-cyclodextrin (CD). The results showed that the presence of CDs reduced the gold nanoparticle size significantly irrespective of the reducing agent used (from 14 to 7 nm for sodium citrate and from 7 to 4 nm for sodium borohydride). The size of the gold nanoparticles was dependent on the concentration and type of CDs used in the synthesis. The particle size was inversely proportional to the concentration of the hydroxyl groups in the CDs. The gold
nanoparticles decreased from an average size of 13.3 nm to 5.4 nm as the concentration of the CDs increased, with the smallest particles being observed in the presence of γ-CD. Luong and coworkers explained that the size of the gold nanoparticles can be influenced by the hydrophobic interaction between large gold nanoparticles and the hydrophobic interior of the CD toroids.\textsuperscript{155} The γ-CD has 24 hydroxyl groups, more than the other CDs, which can prevent this hydrophobic interaction. The authors suggested that the stabilization and reduction of the gold nanoparticle size may be due to hydrophobic-hydrophobic interactions between the cavity of CDs and gold nanoparticles.

In the past few years, cucurbit[n]uril (CB[n], n= 5~8, 10) also has drawn considerable attention as a family of macrocyclic compounds.\textsuperscript{156-158} Cao and coworkers have reported the fabrication of three well-defined sub-10 nm Pt nanoparticles with distinctive morphologies in the presence of CB[6].\textsuperscript{159} The reduction of Pt precursors by L-ascorbic acid in the presence of CB[6] yielded 5 nm Pt particles with (311) facets. Reduction with ethylene glycol yielded near-spherical structures with 4 nm dimensions and both Pt (200) and (111) facets. In the presence of both ascorbic acid and ethylene glycol, multipod-shaped Pt nanoparticles were produced. They attributed the formation of distinct nanostructures to variations in kinetics with different reducing agents.

The weak interaction and the structural feature (pumpkin-like portal) of CB[6] do not block the active sites on the surface of the metal nanoparticles, which renders them catalytically active.\textsuperscript{158,160} They have demonstrated that CB[6]-Pt nanoparticles exhibited high electrocatalytic activity in methanol oxidation reaction (MOR), where methanol reacts with oxygen to form carbon dioxide and water in the presence of a catalyst. In addition, the presence of CB[6] results in exceptional CO tolerance in methanol or CO oxidation as macrocyclic CB[6] can interact with small molecules such as CO\textsubscript{2}, CH\textsubscript{4}, and CO.\textsuperscript{161} CO arising from MOR is known to be a strong poison for Pt catalyst.\textsuperscript{162} CB[6]-Pt nanoparticles showed outstanding electrocatalytic performance during the methanol oxidation process, and their current density was almost 2-fold higher than commercial Pt/C (86 mA/cm\textsuperscript{2} mg at 0.66 V). The CO tolerance for methanol or CO oxidation was evaluated by the peak current ratio of the forward scan (I\textsubscript{f}) to the backward scan (I\textsubscript{b}). The I\textsubscript{f}/I\textsubscript{b} ratio of CB[6]-Pt nanoparticles (>1.54) were much higher than that of commercial
Pt/C (1.05). After simply adding CB[6] to commercial Pt/C, the $I/I_b$ ratio of commercial Pt/C was 1.30. These results proved that the presence of CB[6] can improve the CO tolerance ability.

Additionally, Cao’s research group has evaluated the catalytic activity and stability of the CB[6]-Pd nanoparticles for the Suzuki cross coupling reaction. The spherical CB[6]-Pd nanoparticles (3 nm in size) with (111) facets showed excellent catalytic performance in the Suzuki cross coupling reaction. In particular, when aryl iodide or bromide was used, high yields of biphenyl (mostly higher than 95%) were obtained in 20 min at mild temperature (40 °C or 60 °C).

With appropriate existing or added functional groups, the interaction of macrocycles with metal nanoparticle surfaces can be modulated. Pastoriza-Santos et al. have synthesized quasi-spherical Au nanoparticles in the presence of ammonium functionalized pillar[5]arene (AP[5]A) through a seeded growth process. In this approach, the size of the spherical Au nanoparticles can be controlled by employing a seeded growth approach. Large spherical particles (up to 120 nm in size) can be obtained through two or three sequential growth steps. Pillar[n]arenes can also act as macrocyclic hosts for guest molecules via noncovalent interactions such as hydrophobic and electrostatic interactions. They successfully showed the binding of guests such as 2-naphthoic acid (with a detection limit of $10^{-6}$ M) and polycyclic aromatic hydrocarbons (with a detection limit of $10^{-8}$ M) to AP[5]A-gold nanoparticles in water via surface enhanced Raman scattering (SERS) detection.

Kaifer and coworkers have shown the synthesis of water-soluble Pt and Pd nanoparticles in the presence of CD functionalized with thiol as a macrocyclic surfactant. They showed that such Pt and Pd nanoparticles are catalytically active in the hydrogenation reaction. This is impressive as Cliffel and coworkers have shown that the nanoparticles passivated with linear thiols show much reduced catalytic activity.

Secchi and coworkers have shown that ligand denticity has an effect on the size of gold nanoparticles. A series of gold nanoparticles were synthesized by using the Brust-Schiffrin two-phase method in the presence of mono-, bi- and tridentate thiolate calix[n]arenes. Bi- and tridentate ligands stabilized gold nanoparticles had smaller core sizes (~1 nm). This may be due to a convergent arrangement of the thiols onto the gold core, which leads to a faster passivation rate as well as inhibited growth of the gold core. Irrespective of the denticity of
ligands, the particles size (3 to 1 nm) was inversely proportional to the ratio of S to Au (3:1, 1:3, and 1:6).

Some studies in the literature have examined the stability of metal nanoparticles stabilized by multidentate ligands and compared to those stabilized by monodentate ligands.\textsuperscript{167,168} Lee and coworkers have shown that the multidentate thiols (tridentate thiols) were much more effective in extracting and dispersing large nanoparticles (>15 nm) in organic solvent (toluene) when compared to monodentate ligands.\textsuperscript{167} They suggested that the multidentate ligands exert an enhanced stabilizing ability via the chelate effect. In a recent report, Graf and coworkers have demonstrated the influence of ligand-denticity on the stability of colloidal solutions.\textsuperscript{168} Not surprisingly, they showed that the multivalent ligands provided a higher resistance to sodium chloride induced nanoparticle aggregation, when compared to monovalent ligands. The authors explained that this may be attributed to the chelate effect of multidentate ligands. Differences in binding denticity have their own advantages and disadvantages. Interestingly, they showed that the monovalent PEG thiol ligands protected the gold colloids better when compared to the di- and trivalent thiol ligands against nucleophilic etching by cyanide. The multivalent ligands that are loosely packed on the surface of gold nanoparticles allow the cyanide anions to attack the gold atoms.

9. Resorcinarene and cavitands

Niederl and Vogel obtained a macrocyclic tetrameric product (Scheme 1a; -R = -CH\(_3\) or -C\(_n\)H\(_{2n+1}\)) from resorcinol and acetaldehyde in aqueous sulfuric acid via a condensation reaction.\textsuperscript{169} Later Högberg obtained two stereoisomeric macrocycles of the same general structure (Scheme 1a; -R = aryl) from resorcinol and several aromatic aldehydes (i.e., benzaldehyde and p-bromobenzaldehyde) under similar reaction conditions.\textsuperscript{170} These macrocycles have been referred to as calix[4]resorcinarenes\textsuperscript{171,172} or Högberg compounds\textsuperscript{170} or simply octols\textsuperscript{173} in the literature. Of late, they are commonly referred to as resorcinarenes.\textsuperscript{173} Resorcinarenes can be prepared easily in high yields without the use of templates or high dilution techniques.\textsuperscript{173} The resorcinol and aldehyde comprise the head and tail of the structure, respectively.\textsuperscript{173} With the use of long alkyl chain aldehydes, resorcinarene can be soluble in even non-polar media (i.e., CCl\(_4\) and CHCl\(_3\)).\textsuperscript{173}
Scheme 1. (a) Synthesis of resorcinarene. Structures of resorcinarene cavitand (b) and resorcinarene cavitand tetraarylthiol (c).

Resorcinarenes have been routinely used as hosts in supramolecular chemistry. Atwood and MacGillivray have shown a chiral spheroidal assembly formed by 60 hydrogen bonds with six C-methylcalix[4]resorcinarenes and eight water molecules (Figure 7). The interior of the assembly exhibits a vast internal volume (1.375 Å³) with a well-defined cavity, which is capable of encapsulating guest molecules. In addition, Rebek and coworkers have shown that resorcinarenes can self-assemble into hexameric molecular capsules through hydrogen bonding of the multiple hydroxyl groups present in the upper rim. These capsules can also encapsulate guest molecules. Shivanyuk has shown complex-within-complex assemblies, highly stable Russian-doll (Matryoshka-doll) complex capsules, using a hexameric resorcinarene nanocapsule. Self-assembled hexameric resorcinarene capsules have a huge internal space.
(~1.4 nm$^3$) which enables them to encapsulate small inclusion complexes formed from calix[4]arene and tetramethylammonium salt.

Figure 7. The chiral spheroidal assembly of resorcinarenes held together by 60 hydrogen bonds: (a) a cross-sectional view and (b) space-filling view.$^{172}$ Reproduced with permission from ref. 140b.

In the early 1980s, Cram and coworkers created macrocyclic "cavitands"$^{178}$ by covalently linking neighboring phenolic hydroxyl groups of resorcinarenes (Scheme 1b).$^{179}$ These molecules naturally possess a concave cavity and can accommodate other small molecules or ions.$^{179}$ Covalent linkage of cavitands yields carcerands or hemicarcerands.$^{180}$ A water-soluble
hemicarcerand is useful in drug delivery and green chemistry applications. Chiral functionalization of resorcinarene cavitands is not common, but known . Placing chiral substituent groups on the upper rim of the resorcinarene is expected to selectively bind guests of suitable size, chirality, hydrophobicity, shape, and surface charge characteristics; and is expected to be useful in separation of pharmaceuticals and enantioselective catalysis. Chirally functionalized resorcinarenes can also be used as catalysts in the enantioselective addition of diethylzinc to benzaldehyde. With appropriate functionalization of either the upper or lower rims, cavitands can lead to the formation of coordination cages and metal complexes. In addition to binding guest molecules, cavitands can also act as pH influenced molecular switches, and optical storage devices.

10. Resorcinarenes as nanoparticle stabilizers

In 1999, Wei and coworkers reported the encapsulation of neutral gold nanoparticles by unmodified resorcinarenes. Later, Balasubramanian et al. showed that resorcinarene thiol passivated Au nanoparticles showed excellent dispersion stability (Scheme 1c). They showed that resorcinarene tetrabenzylthiol can extract gold nanoparticles up to nearly 100 nm in size from an aqueous layer into organic solvents. They have demonstrated that the dispersion stability of gold nanoparticles is dependent on the chemical nature of the resorcinarene headgroups. Due to their unique structure, resorcinarene derivatives can effectively stabilize metal nanoparticles via both ligand passivation and steric stabilization. This strategy has several merits: (1) increased stability by multidentate interaction between the surfactant and nanoparticle surface, (2) a lower ratio of surfactants to nanoparticle due to large macrocyclic headgroups, and (3) increased solubility from the long flexible hydrocarbon tails. The last feature allows the hydrocarbon tails to retain a certain degree of conformational freedom. Note that monodentate linear surfactants such as n-alkanethiols normally pack densely with crystalline order, which leads to poor dispersibility of metal nanoparticles.

Wei and coworkers showed that gold nanoparticles of wide-ranging sizes can be self-assembled into 2-D ordering of nanoparticle arrays in an air-water interface by tetraarylthiolate resorcinarene surfactants. To an aqueous colloidal Au nanoparticle dispersions, resorcinarene tetraarylthiolate resorcinarene surfactants in THF were added and mixed
vigorously. After addition of an equal volume of toluene, tetraarylthiolate resorcinarene passivated gold nanoparticles were prepared and simultaneously these gold nanoparticles self-assembled into films at the biphasic interphase. After removal of organic solvents, these nanoparticle arrays were washed with toluene twice to remove excess surfactants. The clean nanoparticle arrays were redeposited onto an air-water interface. They found such 2-D ordering of nanoparticle arrays and monolayer formation were strongly influenced by the concentration and type of electrolyte such as NaCl and trisodium citrate. They further investigated the self-assembly vis-à-vis extraction of gold nanoparticles by encapsulating them with 8 different resorcinarenes. The nature of the resorcinarene headgroups and the presence of electrolytes such as NaCl and sodium citrate play a major role in determining whether the nanoparticle was extracted or self-organization occurred at the aqueous interface. Resorcinarene thiols with good chemisorption properties result in the self-assembly of well-ordered monolayer nanoparticles. In the presence of resorcinarenes with poor chemisorption properties such as tetra-C-methyl-resorcinarene or octa-O-methyl ether resorcinarene, Au nanoparticles were extracted to the interface and formed multilayers. Further, absorbed electrolytes can confine the surfactant encapsulated nanoparticles, which promotes kinetic aggregation and local 2-D ordering of nanoparticle arrays. The interparticle spacing plays a crucial role in determining the optical properties of the Au nanoparticle arrays.

Resorcinarene amines are capable of phase-transferring a variety of nanodiamonds of various sizes (4 to >100 nm) and shapes from aqueous dispersions into organic phases; and can stabilize the dispersions for several months. In contrast, other amine surfactants including benzylamine, hexylamine, and dimethylaminopyridine could not extract nanodiamonds into the organic phase and cetyltrimethylammonium bromide could only extract them fleetingly. This study clearly demonstrates that both the amine functionality and the macrocyclic resorcinarene skeleton are critical in the phase-transferability of nanodiamonds.

In addition, the long alkyl chain of resorcinarenes have also been functionalized with thiol groups and have formed self-assembled monolayers on gold surfaces. Stirling and Davis have shown that such resorcinarene thiols immobilized on gold can interact with a wide range of substrates. They showed that resorcinarene multilayers can be formed using hydrogen bonding interactions and interdigitation. The resorcinarene monolayer has robustness against a wide
range of chemical treatments and multilayers formed from resorcinarene showed selective adsorption to glutaric acid.\textsuperscript{197}

Resorcinarene based surfactants are expected to avoid close-packing on the surface of nanoparticles due to their large macrocyclic structure. Thereby, nanoparticles will have an increased accessible surface area for the application of catalysis.\textsuperscript{21} Katz and coworkers have developed a fluorescence based assay for measuring the accessible surface area on nanoparticles passivated with resorcinarenes and related molecules using 2-naphthalenethiol as a chemisorptive fluorescent probe.\textsuperscript{153,154} In this assay, the authors take advantage of the quenching of the fluorescence emission of 2-naphthalenethiol upon binding to Au nanoparticles. After a critical concentration of 2-naphthalenethiol, there is a linear increase in the observed fluorescence intensity during the addition of 2-naphthalenethiol to nanoparticles. This critical concentration was used to estimate the accessible surface area of the nanoparticles.

Despite a number of studies on resorcinarene functionalized metal nanoparticles, several fundamental questions still remain:

- Despite the potential advantages, the catalytic activity of resorcinarene stabilized nanoparticles has not been documented.\textsuperscript{21} \textit{Given the excellent stabilizing ability of resorcinarene surfactants for Au}\textsuperscript{191,199} and Co\textsuperscript{200} nanoparticles, can resorcinarene surfactants be employed to stabilize other noble metals such as Pd, Pt, etc. for applications in catalysis?

- Often resorcinarene surfactants have been employed either in their original form or as thiolated cavitands for the passivation of metal nanoparticles. While the former employs an ad hoc Au–O interaction, the latter employs the well-known Au–S interaction. \textit{Can the resorcinarene skeleton be modified to generate other ligands which can interact with nanoparticles via other interactions? Also, can the resorcinarene skeleton be used to improve the stability of weakly binding electrostatic interactions via multidentate interactions?}

- In general the systematic investigations of ligand effects especially those involving macrocyclic surfactants are rather limited. Also, macrocyclic surfactants have not been
widely explored in the synthesis and stabilization of bimetallic nanoparticles. Further, the morphological control of nanoparticles with current macrocyclic ligands remains a challenge. Can multidentate resorcinarene ligands control the morphology and composition of mono- and bi-metallic nanoparticles?

- Can resorcinarene based monomers be employed as building blocks to control the morphology of the resulting polymer? Can such resorcinarene based polymeric ligands be employed as templates for the synthesis, stabilization and assembly of nanoparticles?
CHAPTER 2
SYNTHESIS AND CATALYTIC APPLICATIONS OF MONOMETALLIC NANOPARTICLES PREPARED IN THE PRESENCE OF RESORCINARENE SURFACTANTS

1. Introduction

Platinum (Pt) nanoparticles play a prominent role in catalysis and electrocatalytic applications. The synthesis of Pt nanoparticles with well-defined and controlled shapes is in demand for improving their catalytic activity and selectivity. As mentioned in the Introduction, Pt nanoparticles with distinct shapes show enhanced performance in the fields of catalysis and electrocatalysis. Synthesis of Pt catalysts with complex morphologies (e.g., dendritic/highly branched structures or one-dimensional nanowires/rods) is critical for improving Pt electroactivity.

A number of different approaches have been developed for the synthesis of Pt nanoparticles including alcohol reduction, sonochemical reduction, reverse micelles, electrochemical method, microemulsions, photoreduction process and gamma radiolytic reduction. The two-phase synthesis developed by Brust et al. is one of the simplest and most popular routes to prepare thiol-stabilized metal nanoparticles. However, the synthesis of thiol-stabilized Pt nanoparticles has not been successful under Brust-Schiffrin conditions. Castro et al. demonstrated that the formation of a stable complex between a Pt precursor and a thiol in the organic phase retards the reduction of the Pt precursor by sodium borohydride and consequently prevents the formation of Pt nanoparticles. Thus, use of the Brust-Schiffrin method has failed in previous attempts to synthesize Pt nanoparticles. Castro et al. came up with a modified Brust-Schiffrin route where the order of addition of the reducing agent and the surfactant were switched. This method was able to produce stable and size-controlled nominally spherical Pt nanoparticles.
To achieve anisotropic branching of Pt nanostructures (see Figure 2e and 2f in Chapter 1), four main strategies have been employed: seedless growth, seeded growth, templated growth, and chemical etching.\textsuperscript{212} Seedless synthesis is simple and can be readily scaled up. In this approach, shape selectivity relies on the use of twin defects, ions, and ligands.\textsuperscript{212} Altering the reaction conditions, such as the concentration of the capping agent, reaction time and temperature, can control the crystal twinning and growth kinetics.\textsuperscript{212} The formation of a number of twin planes at an early stage of crystal growth is crucial in determining the formation of the anisotropic branching structures.\textsuperscript{213} Ions can also play a major role in branching.\textsuperscript{214} The ions deposited onto the surface of the metal nanocrystals can act as active sites that induce the anisotropic growth of the metal, leading to branched nanostructures. The use of a specific type of ligand is also very important in controlling the surface growth rate of nanocrystals as they can selectively bind to a particular crystallographic surface.\textsuperscript{215} Such a selective surface binding ligand can facilitate the formation of a branched morphology.

In the seeded growth strategy, pre-synthesized seeds are used as nucleation points, which promote the anisotropic growth of the metal nanostructure.\textsuperscript{212} For example, Cheng and coworkers synthesized branched PtAu\textsubscript{n} nanostructures, where the "\textit{n}" is the number of Au branches.\textsuperscript{216} Au atoms are adsorbed (adatoms) on the pre-existing Pt cubic seeds due to their excellent lattice coherence with each other, and the overgrowth of Au adatoms will then occur to form branches. As the size of the Pt seed increases, the number of Au adatoms that can be deposited, increases due to the reduced steric hindrance. Thus, the number of branches increases. This seeded growth strategy often requires control over the size of the seeds and multiple steps in the synthetic process.\textsuperscript{212}

In the templated growth strategy, the templates can be classified as either hard or soft. Typically, a porous anodic aluminum oxide (AAO) membrane has been used as a hard template in generating anisotropic Pt nanostructures.\textsuperscript{217} Pt metals can be electrodeposited into the porous AAO membrane to form Pt nanowires. After the electrodeposition of Pt, the AAO membrane can be dissolved using 1 M NaOH or H\textsubscript{2}SO\textsubscript{4} solution.

The soft templates involve self-assembled structures such as micelles, inverse micelles, and liposomes.\textsuperscript{218} Song and coworkers showed the synthesis of Pt nanowire networks using a soft
template formed by cetyltrimethylammonium bromide (CTAB) under modified two-phase Brust-Schiffrin conditions.\textsuperscript{219} In a two phase water-chloroform mixture, they suggested that swollen wormlike inverse micelles formed within the droplets of chloroform at a high concentration of CTAB (40 mM) with vigorous stirring. The CTAB molecules residing inside the chloroform droplet were at the interface with water. The Pt salts in water are transferred to the inside of the inverse micelles via electrostatic interaction between the positively charged CTAB molecules and the negatively charged Pt salts. These Pt complexes in the inverse micelles are reduced by the addition of an aqueous sodium borohydride solution. The reduced Pt particles will form nanowire networks by reflecting the micellar network structure. The role of the interconnected wormlike micelles and the rate of stirring are crucial in determining the final morphology of the nanomaterials. The main drawback of the template approach is that it is a tedious and time consuming procedure and require the removal of sacrificial templates.\textsuperscript{217}

In the chemical etching strategy, etchants are employed to selectively dissolve a particular crystallographic facet, resulting in the formation of branched nanostructures.\textsuperscript{212} For example, Xiong \textit{et al.} have demonstrated the effect of changing the amounts of HCl, an etchant, in the formation of branched Pt nanocrystals.\textsuperscript{220} When they heated a mixture containing \(\text{H}_2\text{PtCl}_6\), PVP, KBr, ethylene glycol and water at 116 \(^\circ\text{C}\) in air for 24 h in the absence of HCl, tripodal Pt nanocrystals were obtained. In the presence of HCl, single-crystalline cuboctahedral Pt nanoparticles are formed initially, which eventually grow into multiple branched Pt nanostructures. The number of branches increased from tetrapod to octapod as the amounts of HCl increased from 112.5 to 675 mM.

As described earlier in the Introduction, capping ligands can influence the morphology and chemical reactivity of nanoparticles.\textsuperscript{23} Henry and coworkers\textsuperscript{221} have synthesized Pt nanoparticles using different capping agents such as hexadecylamine and 1,8-diamino-octane. While the long chain amine ligands led to the formation of multipodal nanoparticles, the diamine ligands led to the formation of desert-rose-like polycrystalline nanoparticles.\textsuperscript{221} Hexadecylamine can act as soft templates and kinetically favor the formation of elongated shapes.\textsuperscript{221}

Typically, Pt nanoparticles have been prepared with various stabilizers including polymers, ligands, and surfactants. Such stabilizers can be classified as:
- Oxygen-containing molecules (sodium citrate,\textsuperscript{222,223} carbon monoxide,\textsuperscript{224} and 10-undecenoic acid\textsuperscript{225})

- Nitrogen-containing molecules (tetraalkylammonium,\textsuperscript{226,227} poly(vinyl pyrrolidone) (PVP),\textsuperscript{228} and p-aminobenzenesulfonate\textsuperscript{229})

- Phosphorus-containing molecules (polyphosphate,\textsuperscript{230} and phosphine\textsuperscript{231})

- Sulfur-containing molecules (dodecanethiol,\textsuperscript{35} mercaptosuccinic acid,\textsuperscript{232} octadecanethiol,\textsuperscript{36} and 4-mercaptoaniline\textsuperscript{233})

In addition, ligand concentration can also play a major role in the nanoparticle synthesis.\textsuperscript{221} Huang \textit{et al.} investigated the synthesis of Pt nanoparticles during hydrosilylation reaction between hydrosilane and 1-decene.\textsuperscript{234} Both hydrosilane and 1-decene can act as a capping agent for Pt nanoparticles. They showed that the size of the Pt nanoparticles can be increased with the concentration of hydrosilane.\textsuperscript{234} Despite the numerous literature published on Pt nanocrystals, there are still open questions with regard to the synthesis and the parameters controlling their shape and growth.

The overarching goals of this Chapter are to (1) synthesize catalytic Pt nanoparticles in the presence of multidentate resorcinarene surfactants (Figure 8) (2) probe the effect of the macrocyclic resorcinarene headgroup in determining the size and shape of the Pt nanoparticles (3) evaluate the feasibility of employing the Brust-Schiffrin protocol for the synthesis of nanoparticles and (4) investigate the influence of various ligand headgroups in determining the catalytic activity of Pt nanoparticles. Specifically we have evaluated the influence of strongly binding thiol 4 and weakly binding amine 6 as resorcinarene headgroups. We have successfully shown that resorcinarene surfactants, including thiol, can be employed to synthesize Pt nanoparticles under Brust-Schiffrin reaction conditions. Interestingly, we showed that both these surfactants lead to the formation of anisotropic Pt nanocrystals in the presence of these multidentate resorcinarene surfactants. Remarkably, we demonstrate that highly branched Pt nanoparticles can be obtained in the presence of resorcinarene benzylthiol, and we have also evaluated parameters such as mole ratio of surfactants to Pt precursor, and reaction temperature in determining the morphology of such anisotropic Pt nanoparticles. We have further evaluated
the influence of various resorcinarene headgroups in determining the catalytic performance of these nanocrystals in hydrogenation reactions.

Figure 8. Structure of (a) resorcinarene benzylthiol 4 and (b) resorcinarene amine 6.

2. Experimental section

2.1. General remarks

Hydrogen hexachloroplatinate (Acros Organics, 99.9 %), palladium chloride (Alfa Aesar, 99.9 %), tetraoctylammonium bromide (TOABr) (Alfa Aesar, 98+ %), hexylamine (Alfa Aesar, 99 %), and sodium borohydride (Sigma Aldrich, 98+ %) were used as received without any further treatment. All organic solvents were commercially available and distilled before use. Barnstead Nanopure water (18.2 MΩ • cm) was used for all syntheses. All glassware used was silanized.
2. 2. *Synthesis of tetramethyl resorcinarene I*

To a solution of 2-methyl resorcinol (10.08 g, 81.20 mmol) in ethanol (100 mL) in a three-necked round-bottomed flask, heptanal (13 mL, 93.01 mmol) was added under argon atmosphere. The reaction mixture was cooled to 0 °C and after the addition of HCl (10 mL, 12.1 M) at the same temperature, the reaction mixture was refluxed at 80 °C for 20 h. After cooling to room temperature, the reaction mixture was poured into ice cold water (250 mL). The yellow precipitate obtained was filtered and washed with copious amounts of water until the pH of the filtrate was neutral. The precipitate was dried and re-precipitated with methanol. The product obtained was filtered and dried to yield tetramethyl resorcinarene as a yellow solid (14.00 g, 78 %). $\nu_{\text{max}}/\text{cm}^{-1}$: 3420 (b), 2930, 2850, 1470, 994; $\delta_{\text{H}}$ (400 MHz, Acetone-$d_6$): 8.00 (s, 8H), 7.41 (s, 4H), 4.36 (t, $J = 7.8$ Hz, 4H), 2.28 (q, $J = 6.8$ Hz, 8H), 2.03 (s, 12H), 1.41–1.21 (m), 0.88 (t, $J = 6.8$ Hz, 12H).

2. 3. *Synthesis of tetramethyl resorcinarene cavitan 2*

Tetramethyl resorcinarene 1 (6.03 g, 6.85 mmol) was dissolved in DMF (200 mL) in a pressure vessel. Bromochloromethane (18 mL, 277 mmol) and activated cesium carbonate (34.90 g, 107 mmol) were added and the reaction mixture was stirred at 90 °C for 9 h. The reaction mixture was cooled to room temperature, and then poured into 150 mL of 2 M HCl. The crude product was extracted from the aqueous layer with diethyl ether (4 × 100 mL). The organic phase was washed with 2 M HCl (2 × 100 mL), water (2 × 100 mL) and brine (100 mL) and dried over anhydrous magnesium sulfate. After the removal of the inorganic solid and volatiles, the crude product obtained was purified by column chromatography (5 × 12 cm, 0 – 15 % ethylacetate in hexanes) to yield a white solid (5.41 g, 85 %). $\nu_{\text{max}}/\text{cm}^{-1}$: 2930, 2858, 1470, 978; $\delta_{\text{H}}$ (400 MHz,CDCl$_3$): 6.98 (s, 4H), 5.90 (d, $J = 7.2$ Hz, 4H), 4.76 (t, $J = 8$ Hz, 4H), 4.27 (d, $J = 7.2$ Hz, 4H), 2.21 (q, $J = 6.8$ Hz, 8H), 1.98 (s, 12H), 1.44–1.26 (m), 0.90 (t, $J = 6.8$ Hz, 12H); $\delta_{\text{C}}$ (100 MHz, CDCl$_3$): 153.40, 138.13, 123.81, 117.74, 98.69, 37.17, 32.09, 30.30, 29.75, 28.13, 22.88, 14.28, 10.54.
2. 4. Synthesis of resorcinarene tetrabenzylbromo cavitand 3

To a solution of tetramethyl resorcinarene cavitand 2 (2.12 g, 2.28 mmol) in carbon tetrachloride (76 mL), N-bromosuccinimide (2.47 g, 13.87 mmol) and azo-bisisobutyronitrile (0.39 g, 2.40 mmol) were added and refluxed at 85 °C under argon atmosphere. After 8 h, the reaction mixture was cooled to room temperature and diluted with dichloromethane (230 mL). The reaction mixture was washed with room temperature and diluted with dichloromethane (230 mL). The reaction mixture was washed with water (2 × 150 mL) and dried over magnesium sulfate. After removal of the inorganic solid and volatiles, the crude product obtained was purified by column chromatography (5 × 12 cm, 0 – 6 % ethylacetate in hexanes) to yield the title compound as a white solid (2.60 g, 92 %). \( \nu_{\text{max}}/\text{cm}^{-1}: 2928, 2856, 1587, 1470, 978; \delta_{\text{H}} (400 \text{ MHz}, \text{CDCl}_3): 7.13 (s, 4H), 6.05 (d, J = 6.4 \text{ Hz}, 4H), 4.80 (t, J = 8 \text{ Hz}, 4H), 4.57 (d, J = 6.8 \text{ Hz}, 4H), 4.43 (s, 8H), 2.21 (q, J = 6.4 \text{ Hz}, 8H), 1.43–1.26 (m), 0.90 (t, J = 6.8 \text{ Hz}, 12H); \delta_{\text{C}} (100 \text{ MHz}, \text{CDCl}_3): 153.46, 138.02, 124.44, 120.92, 99.04, 36.79, 31.78, 30.04, 29.41, 27.77, 27.65, 22.99, 22.58, 14.00.

2. 5. Synthesis of resorcinarene benzylthiol 4

To a solution of resorcinarene tetrabenzylbromo cavitand 3 (510 mg, 0.41 mmol) in DMF (27 mL), thiourea (224 mg, 2.94 mmol) was added and refluxed under argon atmosphere for 12 h. After cooling the reaction mixture to room temperature, a degassed 1 M NaOH solution (33 mL) was added, and stirred for an additional 1.5 h at room temperature. Then, it was acidified with conc. HCl (12.1 N, 3 mL) at 0 °C. The reaction mixture was extracted with ethyl acetate (3 × 65 mL) and the combined organic phase was washed with water (3 × 70 mL). After removal of volatiles, the crude product obtained was purified by column chromatography (3 × 11 cm, 0 – 15 % ethylacetate in hexanes and 0.1 % acetic acid) to yield a white solid (0.32 g, 74 %). \( \nu_{\text{max}}/\text{cm}^{-1}: 2928, 2568, 1589, 980; \delta_{\text{H}} (400 \text{ MHz}, \text{CDCl}_3): 7.06 (s, 4H), 5.97 (d, J = 6.8 \text{ Hz}, 4H), 4.75 (t, J = 8 \text{ Hz}, 4H), 4.82 (d, J = 7.2 \text{ Hz}, 4H), 3.60 (d, J = 7.2 \text{ Hz}, 8H), 2.22 (q, J = 7.6 \text{ Hz}, 8H), 1.91 (t, J = 7.2 \text{ Hz}, 4H), 1.46–1.26 (m), 0.90 (t, J = 6.8 \text{ Hz}, 12H); \delta_{\text{C}} (100 \text{ MHz}, \text{CDCl}_3): 152.95, 138.29, 127.32, 119.42, 99.99, 37.14, 32.02, 30.33, 29.67, 28.04, 22.82, 18.32, 14.25.
2. 6. Synthesis of resorcinarene tetrathalimidomethyl cavitand 5

To a solution of resorcinarene tetrabenzylbromo cavitand 3 (1.21 g, 0.972 mmol) in toluene (65 mL), potassium phthalimide (1.10 g, 5.919 mmol) and CTAB (0.21 g, 0.589 mmol) were added and refluxed for a day under argon atmosphere. After cooling to room temperature, the reaction mixture was filtered and the filtrate was diluted with 50 mL of chloroform. After removal of volatiles, the crude product obtained was purified by column chromatography (5 x 12 cm, 0 – 6 % ethylacetate in hexanes) to yield the title compound as a white solid (1.07 g, 73 %). Occasionally, this product required additional purification by column chromatography (4 x 12 cm, 0 – 50 % ethylacetate in hexanes and 0.5 % triethylamine) to eliminate miniscule amounts of aromatic impurities, yielding the title compound as a white solid (0.81 g, 84 %). 

2. 7. Synthesis of resorcinarene amine 6

To a solution of resorcinarene tetraphthalimidomethyl cavitand 5 (0.730 g, 0.485 mmol) dissolved in THF (7 mL), ethyl alcohol (63 mL) and hydrazine monohydrate (0.470 mL, >20 equiv.) were added and refluxed under argon atmosphere for 4 h. The reaction mixture was cooled to room temperature, acidified with conc. HCl (12.1 N, 0.6 mL), and refluxed for an additional hour. To the reaction mixture, aqueous sodium hydroxide solution (15 mL, 2 M) was added, and the white precipitate obtained was filtered and dried to yield the title compound (0.43 g, 89 %).
2. 8. Synthesis of monometallic Pt nanoparticles in the presence of resorcinarene benzylthiol

To an aqueous solution (5 mL) of H₂PtCl₆ (18.3 mg, 0.035 mmol), a solution of tetraoctylammonium bromide (29.2 mg, 0.053 mmol) in chloroform (10 mL) was added and vigorously stirred for 30 min at room temperature under argon atmosphere. During stirring, the color of the aqueous phase changed from yellow to colorless, while that of the organic phase changed from colorless to yellow. The organic phase was separated and a solution of resorcinarene benzylthiol surfactant (9.6 mg, 0.009 mmol) in chloroform (10 mL) was added and stirred for 30 min at room temperature. The reaction mixture was allowed to cool to 0 °C and a freshly prepared solution of sodium borohydride (13.9 mg, 0.367 mmol) in ice cold water (2 mL) was added and vigorously stirred at 0 °C for 2 h under argon atmosphere. The color of the reaction mixture transitioned from yellow to brownish yellow within 20 s after the addition of sodium borohydride. After the reaction, the organic phase was collected and washed with copious amounts of nanopure water (20 mL x 3).

2. 8. 1. Effect of concentration of resorcinarene benzylthiol

To an aqueous solution (5 mL) of H₂PtCl₆ (18.3 mg, 0.035 mmol), a solution of tetraoctylammonium bromide (29.3 mg, 0.054 mmol) in chloroform (10 mL) was added and vigorously stirred for 30 min at room temperature under argon atmosphere. During stirring, the color of the aqueous phase changed from yellow to colorless, while that of the organic phase changed from colorless to yellow. The organic phase was separated and a solution of resorcinarene benzylthiol surfactant (4.8 mg, 0.005 mmol) in chloroform (10 mL) was added and stirred for 30 min at room temperature. The reaction mixture was allowed to cool to 0 °C and a freshly prepared solution of sodium borohydride (14.2 mg, 0.375 mmol) in ice cold water (2 mL) was added and vigorously stirred at 0 °C for 2 h under argon atmosphere. The color of the reaction mixture transitioned from yellow to brownish yellow within 10 s after the addition of sodium borohydride. After the reaction, the organic phase was collected and washed with copious amounts of nanopure water (20 mL x 3).
2. 8. 2. **Effect of concentration of metal precursor**

To an aqueous solution (5 mL) of H$_2$PtCl$_6$ (38.8 mg, 0.075 mmol), a solution of tetraoctylammonium bromide (61.4 mg, 0.112 mmol) in chloroform (10 mL) was added and vigorously stirred for 30 min at room temperature under argon atmosphere. During stirring, the color of the aqueous phase changed from yellow to colorless, while that of the organic phase changed from colorless to yellow. The organic phase was separated and a solution of resorcinarene benzylthiol surfactant (10.1 mg, 0.010 mmol) in chloroform (10 mL) was added and stirred for 30 min at room temperature. The reaction mixture was allowed to cool to 0 °C and a freshly prepared solution of sodium borohydride (28.6 mg, 0.756 mmol) in ice cold water (2 mL) was added and vigorously stirred at 0 °C for 2 h under argon atmosphere. The color of the reaction mixture transitioned from yellow to brownish yellow within 10 s after the addition of sodium borohydride. After the reaction, the organic phase was collected and washed with copious amounts of nanopure water (20 mL x 3).

2. 8. 3. **Effect of Reaction Temperature**

To an aqueous solution (5 mL) of H$_2$PtCl$_6$ (18.3 mg, 0.035 mmol), a solution of tetraoctylammonium bromide (29.0 mg, 0.053 mmol) in chloroform (10 mL) was added and vigorously stirred for 30 min at room temperature under argon atmosphere. During stirring, the color of the aqueous phase changed from yellow to colorless, while that of the organic phase changed from colorless to yellow. The organic phase was separated and a solution of resorcinarene benzylthiol surfactant (9.4 mg, 0.009 mmol) in chloroform (10 mL) was added and stirred for 30 min at room temperature. The reaction mixture was allowed to cool to 0 °C and a freshly prepared solution of sodium borohydride (13.6 mg, 0.360 mmol) in ice cold water (2 mL) was added and vigorously stirred at room temperature for 2 h under argon atmosphere. The color of the reaction mixture transitioned from yellow to brownish yellow within 1 min after the addition of sodium borohydride. After the reaction, the organic phase was collected and washed with copious amounts of nanopure water (20 mL x 3).
2. 9. Synthesis of monometallic Pt nanoparticles in the presence of resorcinarene amine

To an aqueous solution (5 mL) of H$_2$PtCl$_6$ (19.5 mg, 0.038 mmol), a solution of tetraoctylammonium bromide (31.1 mg, 0.057 mmol) in chloroform (10 mL) was added and vigorously stirred for 30 min at room temperature under argon atmosphere. During stirring, the color of the aqueous phase changed from yellow to colorless, while that of the organic phase changed from colorless to yellow. The organic phase was separated and a solution of resorcinarene amine surfactant (6.4 mg, 0.006 mmol) in chloroform (10 mL) was added and stirred for 30 min at room temperature. The reaction mixture was allowed to cool to 0 °C and a freshly prepared solution of sodium borohydride (14.3 mg, 0.378 mmol) in ice cold water (2 mL) was added and vigorously stirred at 0 °C for 2 h under argon atmosphere. The color of the reaction mixture turned from yellow to dark brown within 2 min after the addition of sodium borohydride. After 2 h, the organic phase containing nanoparticles was collected and washed with copious amounts of nanopure water (20 mL × 3).

2. 10. Synthesis of monometallic Pt nanoparticles in the presence of hexylamine

To an aqueous solution (5 mL) of H$_2$PtCl$_6$ (19.5 mg, 0.038 mmol), a solution of tetraoctylammonium bromide (31.5 mg, 0.058 mmol) in chloroform (10 mL) was added and vigorously stirred for 30 min at room temperature under argon atmosphere. During stirring, the color of the aqueous phase changed from yellow to colorless, while that of the organic phase changed from colorless to yellow. The organic phase was separated and a solution of hexylamine (3.32 µL, 0.025 mmol) in chloroform (10 mL) was added and stirred for 30 min at room temperature. The reaction mixture was allowed to cool to 0 °C and a freshly prepared solution of sodium borohydride (14.5 mg, 0.383 mmol) in ice cold water (2 mL) was added and vigorously stirred at 0 °C for 2 h under argon atmosphere. The color of the reaction mixture turned from yellow to dark brown within 1 min after the addition of sodium borohydride. After 2 h, the organic phase containing nanoparticles was collected and washed with copious amounts of nanopure water (20 mL × 3).
2.11. Hydrogenation of allyl alcohol to propanol

To remove excess resorcinarene surfactants in the Pt nanoparticle dispersions, a precipitation-redispersion approach was adopted. The Pt nanoparticles were precipitated by the addition of ethanol to dispersions in chloroform with a chloroform:ethanol ratio of 1:9 and centrifuged at 9 k rpm for 30 min. The precipitate collected was redispersed in CDCl$_3$ for catalysis.

A solution of a measured amount of the catalyst in CDCl$_3$ (2 mL) was stirred in a vial in the presence of hydrogen gas for 20 min. Allyl alcohol (47.4 µL, 0.7 mmol) was added with a micropipette and stirring continued under H$_2$ atm. The reaction mixture was monitored by $^1$H NMR.

2. 12. Characterization

Transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) analysis were carried out in a JEOL JEM-2100F field emission microscope operating at 200 kV equipped with an Oxford INCAx-sight EDS detector and a Gatan SC1000 ORIUS CCD camera (11 megapixel). The nanoparticles dispersed in organic solvent were drop cast on a carbon-coated TEM grid. $d$-spacing of lattice in nanostructures was measured using ImageJ software. All TEM images were obtained from as-prepared nanoparticles without any further purification. UV-vis spectra were recorded on a Cary-5000 UV-Vis-NIR spectrophotometer.

3. Results and discussion

3. 1. Resorcinarene ligand effects on Pt nanoparticle synthesis

Towards evaluating the effect of the headgroup of the resorcinarene surfactant on the synthesis of monometallic Pt nanoparticles, we chose resorcinarene benzylthiol 4 and resorcinarene amine 6 as surfactants. These surfactants were synthesized from methylresorcinol and the details are highlighted in Schemes 2 and 3. Resorcinarene 1 with a C6 chain was synthesized in 78 % yield by the acid-promoted condensation of methylresorcinol and heptanal. It was subsequently converted to the corresponding cavitand 2 in 85 % yield by reacting it with bromochloromethane in the presence of cesium carbonate. The cavitand was brominated with $N$-bromosuccinimide in the presence of AIBN to obtain bromocavitand 3 in 92 % yield, which was converted to the
corresponding thiol 4 in 74 % yield by reacting it with thiourea, as shown in Scheme 2. Resorcinarene amine was synthesized, as shown in Scheme 3. Bromocavitand 3 was converted to the corresponding tetraphthalimide intermediate 5 in 79 % yield which was subsequently converted to the corresponding amine 6 in 89 % yield.

Initially we evaluated the synthesis of the Pt nanoparticles in the presence of resorcinarene benzylthiol using the Brust-Schiffrin method. In a typical synthesis, Pt salts were phase transferred from the aqueous phase to chloroform in the presence of tetraoctylammonium bromide. The extracted Pt salts in chloroform were isolated and reduced with aqueous sodium borohydride solution in the presence of resorcinarene benzylthiol at 0 °C. The reaction was allowed to continue for 2 hours at 0 °C. Immediately after the addition of sodium borohydride the color of the reaction mixture turned gray indicating the formation of nanoparticles. The formation of the nanoparticles is remarkable as Pt salts previously could not be reduced by sodium borohydride in the presence of thiols under Brust-Schiffrin conditions.
The UV-vis spectrum (Figure 9a) of the Pt nanoparticles showed an almost featureless spectrum except for a small peak around 280 nm corresponding to the localized surface plasmon resonance of the Pt metal.\textsuperscript{235}

Remarkably, transmission electron microscopic (TEM) analysis of the product (Figure 9b–f) revealed the presence of bundled nanowire like structures and the presence of one-dimensional nanowires. A closer look at the bundled nanostructures revealed the presence of highly branched nanowires (Figure 9c). The formation of such anisotropic nanowires from Brust-Schiffrin synthesis is notable as even modified Brust-Schiffrin synthesis of Pt nanoparticles (where thiol is added at a later stage) leads to only near spherical nanoparticles with dimensions less than 6 nm.\textsuperscript{43,92} The HRTEM images (Figure 9e and f) of these crystalline nanowires revealed that these nanowires contained portions of highly crystalline regions. Further these nanostructures showed \(d\)-spacings of 2.1 and 1.9 Å, which could be attributed to Pt (111) and (200) planes.\textsuperscript{236}
3. 2. Factors influencing the formation of highly branched monometallic nanoparticles

In general, the shape of the Pt nanoparticles can be controlled by both thermodynamic and kinetic factors such as the reducing agent used, concentration of the capping agent and the metal precursor, solvent, time and temperature.\textsuperscript{203,218} The rate of metal reduction is dependent on the choice of the reducing agent. NaBH\textsubscript{4} as a reducing agent can rapidly reduce Pt precursors into Pt
nanonuclei. The freshly formed nuclei are thermodynamically unstable on account of their high surface energy. Driven by the need to minimize their surface energy, the unstable nuclei tend to grow to form thermodynamically favored shapes or aggregates.\textsuperscript{237,238}

The formation of anisotropic structures under Brust-Schiffrin reaction conditions is rare and the current mechanistic understanding of Brust-Schiffrin reaction cannot provide a satisfactory and complete explanation. However, on the basis of literature reports\textsuperscript{35} and our experimental conditions we can state the following. Pt(IV) could be reduced immediately after the addition of resorcinarene benzylthiol, as the Pt (IV) ion is known to be reduced to Pt (II) in the presence of alkanethiol.\textsuperscript{35} The reduction of Pt(IV) to Pt(II) requires 2 electrons and the oxidation of thiol (to disulfide) can provide 1 electron. In this experiment we have a 1:1 ratio of Pt(IV) and benzylthiol, as we employed \( \frac{1}{4} \) equivalent of resorcinarene benzylthiol surfactant with respect to \( \text{H}_2\text{PtCl}_6 \). Under these reaction conditions we will have a mixture of both Pt(IV) and Pt(II) precursors as only \( \frac{1}{2} \) of the Pt(IV) precursors could ideally be converted to Pt(II). Castro and coworkers have suggested that upon addition of NaBH\(_4\), Pt(IV) could be reduced to Pt(0) in the presence of thiol, while the reduction of a Pt(II)-thiol complex is sluggish.\textsuperscript{35} However, Pt(II) ions can be absorbed on the surface of a pre-formed Pt cluster and eventually reduced on the surface of the pre-formed Pt cluster, thereby the Pt(II) species can contribute to the formation of Pt(0) atoms or adatoms.\textsuperscript{239}

The formation of highly branched Pt nanostructures has been attributed to the generation of a high concentration of Pt adatoms and a low concentration of Pt nuclei during the synthesis.\textsuperscript{240} To form highly branched nanostructures, the generation of adatoms is critical during the synthesis of the nanocrystals. These adatoms can diffuse on the surface of the nanocrystal to adopt low energy configurations, that is, structures favored by thermodynamics.\textsuperscript{204,241}

In order to obtain a better idea about the nature of the Pt species involved in the formation of the nanowires, we evaluated the intermediates formed at various stages by UV-vis spectroscopy (Figure 10). We compared the UV-vis spectra of the phase transferred Pt salts in the presence of both TOABr and the resorcinarene benzylthiol surfactant to that of H\(_2\)PtCl\(_6\) dissolved in water. Close to the literature value of 260 nm,\textsuperscript{205,242} H\(_2\)PtCl\(_6\) dissolved in water showed a \( \lambda_{\text{max}} \approx 262 \) nm (Figure 10a, blue trace in i). On the other hand, the Pt salts phase transferred in the presence of
both TOABr and the resorcinarene benzylthiol surfactant had a $\lambda_{\text{max}} \approx 269$ nm (Figure 10a, green trace in iii). The shift in $\lambda_{\text{max}}$ could be due to a number of reasons including change of solvent, change of oxidation state or coordination around the central metal atom among others. Interestingly, there was no difference in the $\lambda_{\text{max}}$ between the phase transferred Pt salts in the presence of both TOABr and the resorcinarene benzylthiol surfactant (Figure 10a, green trace in iii) and TOABr alone (Figure 10a, red trace in ii). However, there were some key differences in the overall shape of the spectra. To get a better idea about the difference between the two phase transferred Pt salts, we compared the spectrum of phase transferred Pt salts in the presence of both TOABr and the resorcinarene benzylthiol surfactant with the spectra obtained by the arithmetic sum of the phase transferred Pt salts in the presence of TOABr alone and resorcinarene benzylthiol surfactant dissolved in chloroform (Figure 10b, green dotted trace in v). A small yet discernable difference was observed. Further the difference spectra between the phase transferred Pt salts in the presence of both TOABr and resorcinarene benzylthiol surfactant and the arithmetic sum of the phase transferred Pt salts in the presence of TOABr alone and resorcinarene benzylthiol surfactant dissolved in chloroform (Figure 10b, purple dotted trace in vi), revealed a distinct rise in the absorbance between 245 – 261 nm. However, due to limitations imposed by the chloroform cut-off, we could not get a complete picture of this difference. We believe that this feature could perhaps be attributed to the presence of Pt(II) (arising from the reduction of Pt(IV) by the resorcinarene benzylthiol surfactant). Similarly, Xia and coworkers$^{243}$ attributed a peak at 248 nm to the Pt(II) formed from H$_2$PtCl$_6$ during the synthesis of Pt nanowires using the polyol process. In this context, it is worth noting that Crooks and coworkers have shown that the environment around Pt(II) can further influence its exact location in the UV-vis spectrum.$^{244}$
Figure 10. (a) UV-vis spectra of (i) $\text{H}_2\text{PtCl}_6$ dissolved in water, (ii) Pt salts phase transferred into chloroform by TOABr, (iii) Pt salts phase transferred into chloroform by TOABr and resorcinarene benzylthiol, and (iv) resorcinarene benzylthiol dissolved in chloroform. (b) (v) the arithmetic sum of ii + iv and (vi) the difference spectra of iii and v.
We evaluated the influence of the reaction parameters including the concentrations of the resorcinarene surfactant and metal precursor, and the reaction temperature on the formation of these highly branched Pt nanostructures. While keeping the concentration of the Pt precursor constant (at 1.77 mM), the concentration of the resorcinarene benzylthiol was decreased from 0.45 mM to 0.23 mM. This change resulted in a decrease in the overall length of the Pt nanowires (Figure 11a and b). When the thiol concentration decreases, it reduces the proportion of the Pt(II) species in the reaction mixture. The presence of a higher proportion of Pt(IV) in the mixture is expected to lead to an increased amount of Pt nuclei. The combination of increased amounts of Pt(IV) and decreased amount of Pt(II) could be responsible for the observed results and effect on the length of the Pt nanowires.

Upon increasing the concentration of the Pt precursor to 3.75 mM from 1.77 mM, in the presence of 0.48 mM of resorcinarene benzylthiol surfactant, branched nanowires similar to those in Figure 9 were obtained with some differences (Figure 11c and d). While the length of the nanowires was somewhat reduced, these nanocrystals were even more highly branched. The increased branching at higher Pt concentrations is consistent with the observations of Tilley and coworkers. They showed that higher concentrations of Pt precursors leads to the formation of branched Pt nanocrystals, while relatively lower concentrations lead to the formation of polyhedral structures. They observed that the growth rate of Pt nanocrystals is much slower with a low precursor concentration when compared to Pt nanocrystals grown with a high precursor concentration. They suggested that the growth mechanism of branched Pt nanostructures is governed by the growth rate. Consistent with their observation, the higher proportion of Pt(IV) (when compared to Pt(II) in this experiment) and the ensuing higher growth rate could be responsible for the increased branching observed in these structures.

We also probed the influence of temperature in the formation of these nanowires. The TEM analysis (Figure 11e and f) of the synthesis carried out with a Pt precursor concentration of 1.77 mM and resorcinarene benzylthiol surfactant concentration of 0.44 mM at room temperature showed the predominant formation of nanowire bundles. A closer look revealed that these nanowires are of comparable dimensions to those prepared at 0 °C, however with kinks in the structure.
Figure 11. TEM images of Pt nanoparticles prepared under different precursor concentrations and temperature. The molar concentrations are provided within parenthesis. a, b. Resorcinarene benzylthiol (0.23 mM) and H$_2$PtCl$_6$ (1.77 mM) at 0 °C. c, d. Resorcinarene benzylthiol (0.48 mM) and H$_2$PtCl$_6$ (3.75 mM) at 0 °C. e, f. Resorcinarene benzylthiol (0.44 mM) and H$_2$PtCl$_6$ (1.77 mM) at room temperature.
Figure 12. UV-vis spectra of (a) Pt nanoparticles prepared in the presence of resorcinarene benzylthiol surfactant under various conditions and (b) their normalized spectra.
UV-vis spectra (Figure 12) of the Pt nanoparticles prepared under various conditions were almost featureless in all cases, indicating that the Pt precursors were completely reduced. The bands between 300 and 400 nm showed a small difference in slope, conceivably due to the shape difference of each Pt nanoparticle.

In the presence of resorcinarene amine surfactant the TEM images revealed the formation of mostly anisotropic crystalline nanostructures of various shapes including a few vaguely reminiscent of V-like bipodal structures and some short branched string-like structures (Figure 13). These Pt nanoparticles prepared in the presence of resorcinarene amine surfactant are relatively smaller nanoparticles (mostly less than 20 nm) when compared to the Pt nanoparticles (nanowires) prepared in the presence of the resorcinarene benzylthiol surfactant. The formation of such vivid anisotropic structures is impressive as typically amine surfactants are known to yield elongated structures. Indeed when we replaced the resorcinarene amine surfactant with a linear hexylamine, we typically obtained anisotropic polycrystalline nanostructures (Figure 14).
Figure 13. TEM images of Pt nanoparticles prepared with H$_2$PtCl$_6$ (1.88 mM) in the presence of resorcinarene amine surfactant (0.31 mM) at 0 °C.
We tested the Pt nanoparticles prepared in the presence of the thiol and amine functionalized resorcinarene surfactants as catalysts in the hydrogenation of allyl alcohol to propanol. The results are summarized in Table 1. Not surprisingly, Pt nanoparticles prepared in the presence of the relatively weakly binding resorcinarene amine yielded 19.1 % of propanol after 5 h and 100 % after 24 h. However, the Pt nanoparticle catalysts prepared in the presence of resorcinarene benzylthiol, resulted in the conversion of only 2.6 % of the allyl alcohol into propanol after 24 h. Initially, we anticipated that the Pt nanoparticles prepared in the presence of resorcinarene benzylthiol would also be catalytically active as Kaifer and coworkers had shown that Pt nanoparticles stabilized in the presence of thiolated β-cyclodextrin were catalytically active in the hydrogenation of allylamine.\textsuperscript{114} Additionally, based on the work of Katz and coworkers on gold nanoparticles,\textsuperscript{153,154} we expected the Pt nanoparticles prepared in the presence of resorcinarene benzylthiol to have unpassivated surface area. Based on the fluorescence binding assay, they demonstrated that the gold nanoparticles stabilized with the resorcinarene surfactant have accessible surface.\textsuperscript{153,154} This has also been verified in our laboratories on phase transferred Pt nanoparticles.\textsuperscript{247}

Figure 14. TEM images of Pt nanoparticles prepared with H$_2$PtCl$_6$ (1.88 mM) in the presence of hexylamine surfactant (1.26 mM) at 0 °C.
Table 1. Summary of the yield of propanol from the hydrogenation of allyl alcohol with Pt nanoparticle catalysts prepared in the presence of various resorcinarene surfactants.

<table>
<thead>
<tr>
<th>Nanoparticle catalysts</th>
<th>Amount (mg)</th>
<th>Yield (%) for time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resorcinarene benzylthiol-Pt nanoparticles</td>
<td>~ 0.5 mg</td>
<td>2.6 % for 24 h</td>
</tr>
</tbody>
</table>
| Resorcinarene amine-Pt nanoparticles | ~ 0.5 mg | 19.1 % for 5 h
| | | 100 % for 24 h |

Our results suggest that the catalytic activity of the Pt nanoparticles synthesized in the presence of resorcinarene surfactants are dependent on the headgroups of the resorcinarene surfactants and we believe that a strongly binding thiol renders the nanoparticles catalytically inactive.

4. Summary

This work shows that the headgroup of the resorcinarene surfactant plays an important role in the formation of Pt nanoparticles and could lead to the formation of crystalline anisotropic nanostructures. The Brust-Schiffrin reduction of Pt precursors in the presence of a resorcinarene benzylthiol surfactant led to the formation of highly branched nanowires. The effect of the reaction parameters such as concentration of resorcinarene surfactant, metal precursors and temperature on the formation of the nanowires was investigated. Our results show that the concentration of the resorcinarene surfactants and metal precursor plays a major role in the formation of the highly branched Pt nanoparticles. In the presence of the resorcinarene amine surfactant, the Brust-Schiffrin reduction of the Pt precursor results in the formation of both crystalline anisotropic Pt nanoparticles including a few somewhat vaguely reminiscent of V-shaped bipodal nanoparticles and some isotropic nanoparticles. We evaluated the influence of the
headgroup of the resorcinarene surfactants in passivating the Pt nanoparticles by determining their catalytic activity. While the Pt nanoparticles prepared in the presence of resorcinarene amine converted allyl alcohol to propanol almost entirely, Pt nanoparticles prepared in the presence of resorcinarene benzylthiol showed almost negligible catalytic activity. Though both the work of Katz and coworkers\textsuperscript{153,154} and work from our own lab\textsuperscript{247} has confirmed the presence of available unpassivated metal on nanoparticle surfaces upon passivation with resorcinarene benzylthiol surfactant, this work shows that it alone is not sufficient for effective catalysis and that other factors are involved in mediating catalysis.
CHAPTER 3
SYNTHESIS, MECHANISTIC INVESTIGATION AND CATALYTIC APPLICATIONS
OF BIMETALLIC NANOPARTICLES PREPARED IN THE PRESENCE OF
RESORCINARENE SURFACTANTS

1. Introduction

Bimetallic nanoparticles\textsuperscript{6,248} have received extensive attention in recent years due to the possibility of tuning their physical and chemical properties with size, morphology and composition\textsuperscript{249-251} towards a variety of applications.\textsuperscript{75,76} From scientific and technological viewpoints, bimetallic nanoparticles play a prominent role in improving the catalytic properties of metal particles. Bimetallization can enhance catalytic activity due to the synergistic effects;\textsuperscript{252,253} for instance Au-Ag bimetallic nanoparticles showed much better catalytic performance than pure Au and Ag monometallic nanoparticles in catalyzing CO oxidation.\textsuperscript{254}

Bimetallic nanoparticles can be synthesized by a variety of techniques such as co-reduction, successive reduction, and electrochemical synthesis.\textsuperscript{40} Co-reduction is similar to the preparation of monometallic nanoparticles. In this approach two metal salts are reduced in the presence of reducing agents such as NaBH\textsubscript{4} and H\textsubscript{2} gas.\textsuperscript{40,255} Successive reduction is the most suitable method for preparing core-shell bimetallic nanostructures. In this seed-mediated approach, atoms of one metal can be deposited and reduced onto the surface of other preformed monometallic nanoparticles to form bimetallic nanoparticles.\textsuperscript{256,257} The electrochemical approach uses a sacrificial bulk metal anode such as a palladium or nickel sheet, where this bulk metal anode is electrochemically oxidized to generate corresponding metal ions.\textsuperscript{258} These metal ions are subsequently reduced electrochemically to the zero-valent state, which aggregates to form metal nanoclusters. The size of the metal nanoclusters can be controlled by altering the current density.\textsuperscript{259} Using electrochemical methods, Reetz and Helbig reported the synthesis of tetraalkylammonium salt stabilized bimetallic NiPd, FeNi, and CoFe nanoparticles in the size range of 2.5 – 3.5 nm.\textsuperscript{260}
In some synthesis of bimetallic nanoparticles, one of the two metal salts with a higher redox potential will precipitate first to form the core, followed by the reduction of the other metal with a relatively lower redox potential to form a shell.\textsuperscript{261} For example, when Pt and Pd ions are reduced in the presence of poly(N-vinyl-2-pyrrolidone) (PVP),\textsuperscript{27,40} the Pt ions with a higher redox potential are reduced to form neutral Pt atoms faster than the Pd ions. These Pt atoms aggregate to form nanoclusters and function as seeds. The Pd ions are then reduced to form neutral atoms, followed by their deposition on Pt nanocluster seeds to form core-shell bimetallic nanoparticles. This might also be in part due to the weaker interaction between Pt atoms and PVP when compared to Pd atoms and PVP.\textsuperscript{40,262} The successive reduction approach has been successfully employed for the formation of PdPt bimetallic nanoparticles with a Pt core with a Pd shell.\textsuperscript{40}

Toshima and coworkers have modified the successive alcohol reduction process to obtain reversed core-shell structured bimetallic nanoparticles in the presence of hydrogen.\textsuperscript{263} Pd has a higher affinity to adsorb hydrogen than Pt, which results in the formation of Pd-hydrogen bonds, and thereby Pd ions are preferentially reduced into Pd nanoclusters. Pt ions are deposited onto the dispersion of the Pd nanoclusters to form Pd-Pt core-shell nanostructures.

Nuzzo and coworkers reported that polymer stabilized bimetallic Pd and Pt nanoclusters can lead to both Pd-Pt and Pt-Pd core-shell nanoclusters via a seed mediated growth process\textsuperscript{256} and a sacrificial hydrogen strategy.\textsuperscript{263} Polymer capped monometallic (Pd or Pt) nanoparticles are prepared, which serve as the core in the formation of a core-shell nanostructure. These premade monometallic nanoclusters are subsequently coated by pure hydrogen gas, and then added to the solution containing the metal salts (H\textsubscript{2}PtCl\textsubscript{6} or Pd(OAc)\textsubscript{2}) to grow Pt or Pd shells on the surface of the premade monometallic nanoclusters.

The shape of the bimetallic nanoparticle can be controlled via (i) template-based methods (hard and soft template), (ii) homogeneous nucleation, and (iii) heterogeneous nucleation approaches.\textsuperscript{50,264} The hard template method is an effective technique to obtain one-dimensional nanorods\textsuperscript{265,266} or nanowires.\textsuperscript{267} The hard templates include inorganic porous materials such as anodic alumina oxide\textsuperscript{267}, and silica nanotubes,\textsuperscript{268} and can act as a framework for the formation of anisotropic nanostructures. On the contrary, the soft templates typically use surfactant-based
The shape of the self-assemblies plays a crucial role in forming the anisotropic nanoparticles. Homogeneous nucleation methods employ a one-pot synthesis, where nucleation and growth proceeds in the same synthetic step. Single crystalline seed particles must be produced in order for the subsequent growth of these nanoparticles to occur with shape control. Heterogeneous nucleation uses preformed seed particles, where nucleation and growth occur separately. Murphy and coworkers reported the size and shape of nanoparticles can be controlled by using a heterogeneous nucleation method. In this approach, the addition of preformed seed nanoparticles to a growth solution containing a metal precursor and ascorbic acid which is acting as a weak reducing agent, leads to the formation of gold nanorods. The shape of the nanocrystals can be controlled by growth conditions and reaction temperature.

Amongst many, PdPt bimetallic nanoparticles are attractive candidates as catalysts, and have been used in a wide array of reactions ranging from hydrogenation to electrooxidation. Pt and Pd nanocatalysts have also demonstrated their utility in practical applications such as hydrogenation, fuel cells, and petroleum cracking. Pt- and Pd-based catalysts show high electrocatalytic performance in the HOR, the ORR, and the MOR as applied in fuel cell technology.

In solution-phase synthesis, metal nanoparticles such as those formed from noble metals (i.e., Pt, Pd, Au, Ag, etc.) that crystallize in a face-centered cubic structure have no intrinsic driving force to form anisotropic nanostructures. In general, solution phase shape control strategies depend on a stabilizing agent which limits the growth of the nanoparticles in particular directions by being adsorbed to that particular surface of the nanoparticle. Note that recent advances have enabled the synthesis of PdPt nanocubes, nanplates, hollow nanocubes, star shaped decahedrons, nanodendrites, tetrahedrons, and core-shell architectures. These synthetic methods typically involve high temperature reduction of metal salts or the decomposition of organometallic precursors. In spite of the recent advances, the techniques and approaches for shape control are currently underdeveloped in comparison to size-control techniques.

The overall goal of this work is to evaluate the influence of resorcinarene based multidentate surfactants in determining the morphology and composition of bimetallic nanoparticles. Towards
this, we synthesized PdPt bimetallic nanoparticles in the presence of resorcinarene amine and thiol surfactants via the Brust-Schiffrin biphasic reduction. This work shows that anisotropic bipodal nanoparticles of tunable composition can be prepared in the presence of resorcinarene surfactants.

2. Experimental section

2.1. General remarks

Hydrogen hexachloroplatinate (Acros Organics, 99.9 %), palladium chloride (Alfa Aesar, 99.9 %), hexylamine (Alfa Aesar, 99 %), tetaoctylammonium bromide (TOABr) (Alfa Aesar, 98+ %), and sodium borohydride (Sigma Aldrich, 98+ %) were used as received without any further treatment. All organic solvents were commercially available and distilled before use. Barnstead Nanopure water (18.2 MΩ • cm) was used for all syntheses. All glassware was silanized.

2.2. Synthesis of resorcinarene benzylthiol 4

Please refer to Chapter 2.2.5 for the synthesis of resorcinarene benzylthiol 4 and associated characterization.

2.3. Synthesis of resorcinarene amine 6

Please refer to Chapter 2.2.7 for the synthesis of resorcinarene amine 6 and associated characterization.

2.4. Synthesis of bimetallic (PdPt) nanoparticles in the presence of resorcinarene benzylthiol surfactant 4

To an aqueous solution (5 mL) of H2PtCl6 (9.75 mg, 0.019 mmol) and H2PdCl4 [prepared by dissolving PdCl2 (3.5 mg, 0.020 mmol) in HCl (230 µL of 0.2 N)], a solution of tetaoctylammonium bromide (31.0 mg, 0.057 mmol) in chloroform (10 mL) was added and vigorously stirred for 30 min at room temperature under argon atmosphere. During stirring, the color of the aqueous phase changed from yellow to colorless, while that of the organic phase changed from colorless to reddish brown. The organic phase was separated and a solution of resorcinarene benzylthiol 4 (6.9 mg, 0.006 mmol) in chloroform (10 mL) was added and stirred
for 30 min at room temperature. The reddish brown organic phase immediately became yellowish brown. The reaction mixture was allowed to cool to 0 °C and a freshly prepared solution of sodium borohydride (14.6 mg, 0.386 mmol) in ice cold water (2 mL) was added and vigorously stirred at 0 °C for 2 h under argon atmosphere. The color of the reaction mixture transitioned from yellowish brown to black within 10 s after the addition of sodium borohydride. After the reaction, the organic phase was collected and washed with copious amounts of nanopure water (20 mL x 3).

Such as-prepared nanoparticles were further purified by a precipitation-redispersion cycle. For precipitation, nanoparticle dispersions in chloroform were mixed with isopropyl alcohol (a poor solvent) in a 1:2 volume ratio and centrifuged at 10000 rpm for 20 min. The introduction of a more polar and poor solvent (i.e., isopropyl alcohol) into resorcinarene surfactant capped bimetallic nanoparticles with nonpolar hydrocarbon tailgroups leads to the precipitation of nanoparticles. The precipitate obtained after decanting the supernatant could be readily redispersed in chloroform by gentle shaking.

2. 5. Synthesis of bimetallic (PdPt) nanoparticles in the presence of resorcinarene amine surfactant 6

To an aqueous solution (5 mL) of H₂PtCl₆ (9.75 mg, 0.019 mmol) and H₂PdCl₄ [prepared by dissolving PdCl₂ (3.5 mg, 0.020 mmol) in HCl (230 μL of 0.2 N)], a solution of tetraoctylammonium bromide (31.1 mg, 0.057 mmol) in chloroform (10 mL) was added and vigorously stirred for 30 min at room temperature under argon atmosphere. During stirring, the color of the aqueous phase changed from yellow to colorless, while that of the organic phase changed from colorless to reddish brown. The organic phase was separated and a solution of resorcinarene amine surfactant 6 (6.2 mg, 0.006 mmol) in chloroform (10 mL) was added and stirred for 30 min at room temperature. The reddish brown organic phase immediately became yellowish brown. The reaction mixture was allowed to cool to 0 °C and a freshly prepared solution of sodium borohydride (14.5 mg, 0.383 mmol) in ice cold water (2 mL) was added and vigorously stirred at 0 °C for 2 h under argon atmosphere. The color of the reaction mixture transitioned from yellowish brown to black within 10 s after the addition of sodium borohydride.
After the reaction, the organic phase was collected and washed with copious amounts of nanopure water (20 mL x 3).

2. 6. *Synthesis of monometallic Pt nanoparticles in the presence of resorcinarene amine 6*

Please refer to Chapter 2. 2. 9. for the synthesis of monometallic Pt nanoparticles in the presence of resorcinarene amine surfactant 6.

2. 7. *Synthesis of monometallic Pd nanoparticles in the presence of resorcinarene amine 6*

To a solution of H₂PdCl₄ [prepared by dissolving PdCl₂ (13.4 mg, 0.075 mmol) in HCl (900 µL of 0.2 N)], a solution of tetraoctylammonium bromide (62.4 mg, 0.114 mmol) in chloroform (20 mL) was added and vigorously stirred for 30 min at room temperature under argon atmosphere. During stirring, the color of the aqueous phase changed from reddish brown to colorless, while that of the organic phase changed from colorless to reddish brown. The organic phase was separated and a solution of resorcinarene amine surfactant 6 (12.6 mg, 0.013 mmol) in chloroform (20 mL) was added and stirred for 30 min at room temperature. The reaction mixture was allowed to cool to 0 °C and a freshly prepared solution of sodium borohydride (28.6 mg, 0.756 mmol) in ice cold water (4 mL) was added and vigorously stirred at 0 °C for 2 h under argon atmosphere. The reddish brown organic phase immediately became black after the addition of sodium borohydride. After the reaction, the organic phase was collected and washed with copious amounts of nanopure water (40 mL x 3).

2. 8. *Synthesis of bimetallic nanoparticles with linear surfactant (1-hexylamine)*

To an aqueous solution (5 mL) of H₂PtCl₆ (9.75 mg, 0.019 mmol) and H₂PdCl₄ [prepared by dissolving PdCl₂ (3.5 mg, 0.020 mmol) in HCl (230 µL of 0.2 N)], a solution of tetraoctylammonium bromide (31.0 mg, 0.057 mmol) in chloroform (10 mL) was added and vigorously stirred for 30 min at room temperature under argon atmosphere. During stirring, the color of the aqueous phase changed from yellow to colorless, while that of the organic phase changed from colorless to reddish brown. The organic phase was isolated and a solution of 1-hexylamine (3.32 µL, 0.025 mmol) in chloroform (10 mL) was added and stirred for 30 min at room temperature. The reaction mixture was allowed to cool to 0 °C and a freshly prepared solution of sodium borohydride (14.7 mg, 0.388 mmol) in ice cold water (2 mL) was added and
vigorously stirred at 0 °C for 2 h under argon atmosphere. The color of the reaction mixture transitioned from yellow to black within 10 s after the addition of sodium borohydride. After the reaction, the organic phase was collected and washed with copious amounts of nanopure water (20 mL x 3).

2. 9. Synthesis of bimetallic nanoparticles by a reversed Brust-Schiffrin two-phase system

The bimetallic nanoparticles in the reversed Brust-Schiffrin synthesis were prepared by a literature procedure.97 To an aqueous solution (5 mL) of H₂PtCl₆ (9.75 mg, 0.019 mmol) and H₂PdCl₄ [prepared by dissolving PdCl₂ (3.34 mg, 0.019 mmol) in HCl (224 µL of 0.2 N)], a solution of tetraoctylammonium bromide (31.0 mg, 0.057 mmol) in chloroform (10 mL) was added and vigorously stirred for 30 min at room temperature under argon atmosphere. During stirring, the color of the aqueous phase changed from yellow to colorless, while that of the organic phase changed from colorless to reddish brown. The organic phase was separated, and chloroform (8 mL) was added and stirred for 30 min at room temperature. The organic phase was allowed to cool to 0 °C and a freshly prepared solution of sodium borohydride (14.6 mg, 0.386 mmol) in ice cold water (2 mL) was added. The color of the reaction mixture changed from reddish brown to black within 10 s after the addition of sodium borohydride. With a time delay of 10 s or 5 min, a solution of resorcinarene amine surfactant 6 (6.2 mg, 0.006 mmol) in chloroform (2 mL) was added and vigorously stirred at 0 °C for 2 h under argon atmosphere. After the reaction, the organic phase was collected and washed with copious amounts of nanopure water (20 mL x 3).

2. 10. Synthesis of bimetallic nanoparticles by a monophasic approach

An aqueous solution (5 mL) of H₂PtCl₆ (9.75 mg, 0.019 mmol) and H₂PdCl₄ [prepared by dissolving PdCl₂ (3.34 mg, 0.019 mmol) in HCl (224 µL of 0.2 N)] was vigorously stirred with a chloroform (10 mL) solution containing TOABr (31.1 mg, 0.057 mmol) for 30 minutes. The organic phase containing metal salts was separated, evaporated, and subsequently dried under vacuum for 2 days. The TOA stabilized metal salt residue was dissolved in chloroform (10 mL) and a solution of resorcinarene amine (6.3 mg, 0.006 mmol) in chloroform (5 mL) was added to it and stirred at room temperature for 30 min. The reaction mixture was cooled to 0 °C and tetrabutylammonium borohydride (96.9 mg, 0.377 mmol) in chloroform (7 mL) was added under
argon atmosphere. Almost immediately after the addition of the reducing agent, the reaction mixture turned black. After stirring for 2 h at 0 °C, the reaction mixture was subsequently washed with water (20 mL x 3).

2. 11. Suzuki cross-coupling reaction

To a dispersion of phenyl boronic acid (18.2 mg, 0.149 mmol), iodobenzene (0.01 mL, 0.098 mmol), and K$_2$CO$_3$ (27.2 mg, 0.197 mmol) in toluene (9 mL), (PdPt, Pt or Pd) metal nanoparticles (0.6 mg metal content) prepared in the presence of resorcinarene amine surfactant 6 in chloroform (3 mL) were added and refluxed for 2 days. The product formation was analyzed by HPLC analysis.

2. 12. Dynamic light scattering (DLS) sample preparation

In order to prepare the inverse micelles from either TOABr alone or a mixture of TOABr and resorcinarene amine surfactant, a solution of TOABr in chloroform (6.2 mg, 0.011 mmol, 2 mL) was mixed with water (1 mL) and stirred at room temperature for 30 min. The organic layer was separated and either a resorcinarene amine solution in chloroform (1.3 mg, 0.0013 mmol, 2 mL) or chloroform (2 mL) was added, stirred at room temperature for 30 min, and used as such for DLS measurements.

2. 13. Characterization

Transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) analysis were carried out using a JEOL JEM-2100F field emission microscope operating at 200 kV equipped with an Oxford INCAx-sight EDS detector and a Gatan SC1000 ORIUS CCD camera (11 megapixel). The nanoparticles dispersed in organic solvent were drop cast on a carbon-coated TEM grid. d-spacing of lattice in nanostructures and the dimensions of nanoparticles were measured using ImageJ software. Unless otherwise mentioned as as-prepared samples, all TEM images were obtained from precipitated and redispersed (purified) nanoparticles. UV-vis spectra were recorded on a Cary-5000 UV-Vis-NIR spectrophotometer. DLS analysis was carried out at 25 °C in a Malvern Zetasizer ZEN 3200 model. $^1$H-NMR spectra were recorded on a Varian 400 MHz instrument. High performance liquid chromatography (HPLC) analysis of catalytic reactions was carried out in a Thermoelectron spectrum HPLC equipped with a PDA detector.
and C18 functionalized Hypersil gold column (250 x 4.6 mm dimension, 5 mm particle size) using 60% CH$_3$CN/H$_2$O (1 mL/min) as the mobile phase. Unless otherwise explicitly stated, all data provided are from purified samples.

3. Results and discussion

A modified Brust-Schiffrin protocol$^{94}$ was employed for the synthesis of PdPt bimetallic nanoparticles in the presence of resorcinarene surfactants. Pd and Pt metal salts dissolved in water were phase transferred into chloroform with the aid of tetraoctylammonium bromide. The organic phase containing the metals salts were separated, treated with resorcinarene surfactants, and reduced at 0 °C with aqueous sodium borohydride. The nanoparticles thus obtained were purified by a precipitation-redispersion technique. The bimetallic nanoparticles in chloroform were precipitated by the addition of 2-propyl alcohol in a 1:2 ratio. The suspension was centrifuged at 10K rpm for 20 min at room temperature. After removal of supernatant, the precipitate obtained could be readily redispersed in chloroform by gently shaking.

The UV-vis spectra of the PdPt nanoparticles indicated an almost featureless spectrum with the exception of a shoulder around 280 nm (Figure 15). UV-vis spectra has played a significant role in the characterization of metal nanoparticles.$^{281}$ The localized surface plasmon resonance (LSPR) of noble metal nanoparticles is dependent on their size, shape, environment parameters such as surfactant and dispersed solvent, and aggregation.$^{281,282}$ Unlike Au and Ag nanoparticles with their LSPR in the visible region, in the case of monometallic Pt and Pd the LSPR peak is typically centered in the UV region (near 200 nm).$^{281}$ UV-vis spectrum of precipitated and redispersed (purified) nanoparticles, though featureless, differed somewhat from the as-prepared samples (Figure 15). It must be mentioned that the UV-vis spectra of PdPt bimetallic nanoparticles have been shown to be sensitive to the relative ratio of Pt and Pd, and larger, anisotropic monometallic nanostructures have tunable absorption in the visible region.$^{282}$
Transmission electron microscopy (TEM) analysis was employed for the morphological characterization of these nanoparticles. Bimetallic PdPt nanoparticles prepared in the presence of resorcinarene benzylthiol surfactant showed mostly spherical nanoparticles along with a few random anisotropic structures (Figure 16). Despite the excellent miscibility of Pt and Pd, the EDS analysis of the anisotropic nanoparticles formed in the presence of resorcinarene...
benzylthiol revealed that only Pt was present (Figure 16c). In addition to Pt and Pd, we also observed Cu originating from the grid.²⁸³

Figure 16. TEM (a–b) and EDS (c) of PdPt nanoparticles prepared in the presence of resorcinarene benzylthiol.
In the case of resorcinarene amine surfactant, the anisotropic shaped nanoparticles obtained revealed that greater than 80% of them (from n > 250 particles) had a V-shape or a variant on the V-shape such as wide V or U, one-arm bent-V, or both arms bent-V shaped nanoparticles (Figure 17) and Figure 18 shows the distribution of anisotropic structures from both as-prepared and purified samples. When compared to as-prepared bimetallic nanoparticles, the purified samples contain more of the V-shaped and one-arm bent V-shaped nanoparticles. During the precipitation–redispersion cycle, relatively larger and heavier anisotropic V-shaped nanoparticles can be preferentially sedimented and separated by centrifugation. This observation is remarkable as typical solution based synthesis of branched nanocrystals tends to produce mixtures of multipods.\textsuperscript{213} The lengths of the V-shaped arms were often asymmetrical. The lengths of the shorter and longer arms were 8.4 ± 2.4 nm and 10.0 ± 2.7 nm respectively. The ratio of the lengths shorter to longer in each nanoparticle was found to be 1.2 ± 0.15 (n = 75). The cross-sectional analysis of the arms indicated a width of 2.6 ± 0.4 nm. Consistent with Pt and Pd (111) planes, HRTEM analysis of these crystalline nanoparticles presented d-spacing of 0.23 nm.\textsuperscript{284} The selected area electron diffraction (SAED) pattern of the bimetallic V-shaped PdPt nanoparticles were identified as Pt or Pd (111), (200), (220), (311) and (222) planes (Figure 17f).
Figure 17. TEM (a–e) and SAED (f) of PdPt nanoparticles prepared in the presence of resorcinarene amine.
Figure 18. Histogram of anisotropic nanostructures in as-prepared (solid bars) and purified (patterned bars) PdPt bimetallic nanoparticles prepared at 0 °C in the presence of resorcinarene amine surfactant: 1. V, 2. one-arm bent V, 3. both arms bent V, 4. wide open V, 5. U 6. linear and 7. triangular shaped nanoparticles.
Energy dispersive spectroscopy (EDS) was employed to analyze the metal content in these bimetallic nanoparticles. In contrast to the 1:1 ratio of Pt:Pd employed in the synthesis, the V-shaped nanoparticle obtained in the presence of resorcinarene amine was enriched in Pt and showed a Pt:Pd ratio of 7.6 (Figure 19a). In contrast, the spherical nanoparticles produced in the same synthesis showed a Pt:Pd ratio of 0.75 (Figure 19b). The higher Pt content in V-shaped nanoparticles was widely prevalent and reproducible. Eight anisotropic nanoparticles from four different synthetic preparations showed a Pt:Pd ratio of 8.7 ± 2.9. It is noteworthy that there were no significant differences in the Pt:Pd ratio of the anisotropic nanoparticles in as-prepared (9.9 ± 2.1) and purified (8.0 ± 3.3) samples.
Figure 20. STEM spot analysis of anisotropic V-shaped nanoparticles prepared in the presence of resorcinarene amine.

The uniformity of the distribution of Pt and Pd was evaluated by EDS analysis at distinct spots of the anisotropic V-shaped nanoparticles (with a beam spot size of 0.5 nm) under scanning transmission electron microscopy (STEM) mode. The ratio of Pt:Pd was analyzed at the center, and at the end of both arms. The analysis revealed a relatively lower Pt:Pd ratio at the center than at the end of both arms (Figure 20). The Pt:Pd ratio on both arms were not identical, and in all cases but one the shorter arm had a relatively higher ratio of Pt:Pd than the longer arm. The analysis of 5 different anisotropic structures gave a Pt:Pd ratio of 3.9 ± 0.8 at the center of the V-shaped nanoparticle, 6.9 ± 2.3 at the end of the relatively shorter arm and 5.6 ± 3.2 at the end of the relatively longer arm.

It is known that the stabilization of bimetallic PdPt nanoparticles by linear amines is ineffective and typically leads to the formation of superstructures. Notably, the dispersions of bimetallic PdPt nanoparticle prepared in the presence of resorcinarene amine remained stable without any
noticeable sedimentation even after several months (Figure 21). Also, consistent with literature, the dispersions of the Pd and Pt nanoparticles prepared in the resorcinarene benzylthiol were stable (not shown). We did not observe any visible sedimentation or changes in the UV-vis spectra in both cases.

Figure 21. PdPt nanoparticle dispersions prepared in the presence of resorcinarene amine (~4 months).

3.1. Factors influencing the formation of V-shaped nanoparticles

The dominant formation of bipodal, V-shaped structures in the presence of resorcinarene amine under Brust-schiffrin conditions is noteworthy and required additional probing. To probe the importance of the resorcinarene surfactant in the synthesis of bipodal nanoparticles, it was replaced with a linear surfactant, 1-hexylamine. The resulting nanoparticles were less stable when compared to nanoparticles prepared in the presence of resorcinarene amine surfactant.
Noticeable amount of precipitate were observed at the end of the synthesis. The TEM analysis of the resulting bimetallic nanoparticles (Figure 22a) showed mostly spherical and some elongated nanostructures. Unlike the resorcinarene amine surfactant, the nanoparticles prepared in the presence of hexylamine had a Pt:Pd ratio of \(~1\) (Figure 22b). These observations are consistent with the literature, as the coreduction of Pt and Pd precursors with commonly employed surfactants such as PVP\textsuperscript{285} or oleylamine\textsuperscript{286} also resulted in the formation of much smaller, spherical nanoparticles. Given this background, we probed the formation of the V-shaped nanoparticles in the presence of resorcinarene amine in detail.
In the bimetallic nanoparticle synthesis, both V-shaped anisotropic and spherical nanoparticles are observed concurrently as early as 5 min (Figure 23). Further, even after 2 h, spherical nanoparticles were still present. There are differences between the width of the bipodal PdPt nanostructures (2.6 ± 0.4 nm) and the dimensions of the spherical PdPt nanoparticles (2.0 ± 0.4 nm). Given this background, both of them may be formed concurrently from homogeneous nucleation events. Even though such a nucleation event is often not invoked for the formation of
branched structures, recently Xia and coworkers have shown that both homogeneous and heterogeneous nucleation events lead to the formation of dendritic bimetallic nanostructures.\textsuperscript{85,287,288}

Figure 23. TEM of PdPt nanoparticles prepared in the presence of resorcinarene amine surfactant at 0 °C after 5 min of reaction.

In the literature, the presence of a second metal or foreign ion has been implicated in the formation of anisotropic nanoparticles.\textsuperscript{289} To probe the importance of Pd vis-à-vis Pt in the formation of bipodal nanoparticles, monometallic Pt and Pd nanoparticles were synthesized in the presence of resorcinarene amine surfactant under identical conditions. All detailed monometallic Pt nanoparticle results are described on Chapter 2. As shown in Figure 13 in
Chapter 2, TEM analysis of the synthesized Pt nanoparticles revealed the formation of somewhat V-like crystalline nanoparticles. In the case of Pd nanoparticles, mostly spherical nanoparticles along with very few polycrystalline V-shaped nanoparticles were obtained (Figure 24a and b). It is worth noting that a larger proportion of anisotropic nanostructures (when compared to spherical nanoparticles) were formed in the case of Pt than in Pd. These experiments reveal that the dominant formation of the V-shaped nanoparticles requires the presence of both Pt and Pd.

![Figure 24. TEM monometallic Pd (a–b) nanoparticles prepared in the presence of resorcinarene amine surfactant.](image)

Previously, the seed mediated approach has been employed in the synthesis of branched nanoparticles.\textsuperscript{290,291} Our STEM spot analysis (Figure 20) showed a relatively lower Pt:Pd ratio (3.9 ± 0.8) at the center of V-shape nanoparticles and Pt rich arms. To test if the V-shaped nanoparticles can grow from Pd nanoparticle seeds, Pt salts were reduced in the presence of Pd monometallic nanoparticle seeds at both 0 °C and at room temperature. Both these syntheses
predominantly yielded spherical nanoparticles (Figure 25a and b), ruling out the formation of bipodal PdPt nanoparticles via Pd seeds. These results are consistent with the observations of Tilley and coworkers,\textsuperscript{292} who have shown that amine ligand stabilized Pd nanoparticle seeds retain their morphology during subsequent growth stages.

![Figure 25. TEM of bimetallic PdPt nanoparticles prepared in the presence of resorcinarene amine surfactant at (a) 0 °C and (b) room temperature with monometallic Pd nanoparticle seeds.](image)

Temperature can significantly influence the formation of nanoparticles.\textsuperscript{92,272,293} To probe the influence, if any, of the temperature in determining the morphology and composition of the V-shaped nanoparticles, the PdPt nanoparticle synthesis was carried out at room temperature. Though the bipodal morphology could be replicated even at room temperature, the Pt:Pd ratio was only 5.6 ± 1.1 (Figure 26).
In order to investigate the effect of the oxidation state of the Pt precursor on the formation of the anisotropic nanoparticles, the bimetallic nanoparticle synthesis was carried out using $\text{K}_2\text{PtCl}_4$ instead of $\text{H}_2\text{PtCl}_6$. Irrespective of the oxidation state of Pt, anisotropic bipodal Pt rich nanoparticles and isotropic Pd rich nanoparticles were obtained. EDS analysis indicated that the anisotropic nanoparticles synthesized in this experiment had a Pt:Pd ratio of $13.9 \pm 2.6$ (Figure 27).
To evaluate the influence of the feed ratio of Pt:Pd precursors in determining the morphology and composition of anisotropic nanoparticles, PdPt nanoparticle synthesis was carried out with a Pt:Pd precursor ratio of 3:1 with all other conditions being identical. The TEM analysis (Figure 28) showed the presence of mostly spherical nanoparticles along with a few V-like nanoparticles. The EDS analysis of 3 different V-shaped nanoparticles gave a Pt:Pd ratio of 33.0 ± 10.6. This experiment reveals the importance of feed ratio in determining the proportion of anisotropic structures formed under these conditions and further the composition of PdPt in the anisotropic bimetallic nanoparticles can indeed be altered by varying the feed ratio.
In the biphasic reaction leading to V-shaped nanoparticles, after the phase-transfer of the metal salts into the organic layer, the aqueous layer is removed during the nanoparticle synthesis. There are reports in the literature where the aqueous phase is not removed at this stage.\textsuperscript{34} After the phase-transfer of nanoparticles the remaining aqueous phase is typically acidic in nature. To test if a residual amount of acid (from the aqueous phase) is important in the formation of V-shaped nanoparticles, two different syntheses were carried out: 1. In one reaction the aqueous phase was not removed from the organic phase and 2. In another reaction, after the removal of the aqueous phase, the organic phase was washed thrice with copious amounts of water. TEM analysis of both these reactions are provided in Figure 29. The 1\textsuperscript{st} reaction resulted in mainly spherical nanoparticles, while the formation of the V-shaped nanoparticles was unaffected in the 2\textsuperscript{nd} reaction. These experiments indicate that the successful synthesis of bipodal V-shaped structures requires the removal of the aqueous phase prior to reduction, and that the acid generated during phase transfer must be entirely removed from the synthesis.

Figure 28. TEM images of PdPt nanoparticles prepared in the presence of resorcinarene amine surfactant with a Pt:Pd precursor feed ratio of 3:1.
Figure 29. TEM of PdPt nanoparticles prepared in the presence of resorcinarene amine surfactant (a) with the original aqueous phase after the phase-transfer of metal salts and (b) after the removal of aqueous phase.

3.2. Mechanistic studies on the formation of V-shaped nanoparticles

Having established the requirement of resorcinarene amine surfactant in the synthesis of bipodal V-shaped nanoparticles, we probed the mechanism of its formation in detail. From a mechanistic point of view, the Brust-Schiffrin reaction has been significantly probed in recent years.

To test the importance of water in the formation of V-shaped bimetallic nanoparticles, a monophasic synthesis was carried out in the absence of water. The metal salts phase-transferred into the organic phase were concentrated and dried under vacuum, dissolved in dry chloroform and reduced with tetrabutylammonium borohydride. The TEM analysis (Figure 30) showed the presence of mostly spherical nanoparticles along with a few elongated structures. This experiment clearly establishes that in addition to resorcinarene amine surfactant, water and hence inverse micelles are also required for the formation of the V-shaped bimetallic nanoparticles.
To probe the importance of the order of addition of the reagents, a reversed Brust-Schiffrin synthesis was carried out. In contrast to conventional Brust-Schiffrin syntheses, in this method, the surfactant is added to the reaction mixture after the addition of the aqueous sodium borohydride. Two reversed Brust-Schiffrin experiments were performed with a delay time of 10 s and 5 min. In the case of the 5 min delay, a noticeable amount of insoluble matter was observed after the reaction. The 10 s delay resulted in significant amounts of V-shaped nanoparticles (Figure 31a). In contrast, in the case of the 5 min delay, only a few anisotropic structures that vaguely resemble V-shaped nanoparticles were produced (Figure 31b). Furthermore, the crystallinity of the nanoparticles was considerably different between these two syntheses. While the anisotropic bimetallic nanoparticles formed with a 10 s delay time were crystalline, the nanoparticles obtained with a 5 min delay were polycrystalline. The single particle EDS analysis of the V-shaped nanoparticles obtained from the 10 s delay reaction showed a Pt:Pd ratio of $5.5 \pm 0.6$ ($n = 3$) (Figure 31c). In the case of the 5 min delay reaction, the anisotropic nanoparticle analyzed showed a Pt:Pd ratio of $0.9 \pm 0.3$. These experiments demonstrate the crucial role played by the resorcinarene amine surfactant in determining the shape, composition and crystallinity of the anisotropic bimetallic nanoparticles formed under Brust-Schiffrin conditions.
Further this experiment provides indirect evidence that resorcinarene amine is part of the inverse micelle nanoreactor and not a passive bystander during the bimetallic nanoparticle synthesis. In contrast to our experiment, Tong and coworkers showed the synthesis of nominally spherical gold nanoparticles with 2.5 ± 0.7 nm (10 s delay time) in size in the presence of dodecanethiol under the reversed Brust-Schiffrin conditions. They suggested that the organo-chalcogen ligands present outside the inverse micelles prior to reduction merely control the size of gold nanoparticles after reduction.

Figure 31. TEM images and (c) EDS data of PdPt nanoparticles prepared by reversed Brust-Schiffrin synthesis with a 10 s (a) and 5 min (b) delay.
To obtain direct evidence on the nature of the inverse micelle, dynamic light scattering (DLS) analysis was carried out under a variety of conditions. Though a single peak was obtained in the case of experiments carried out with TOABr and a mixture of TOABr and resorcinarene amine surfactant there were drastic differences in the size of the inverse micelles (Figure 32 red and blue lines). Similar experiments were also carried out in the presence of metal salts (Figure 32 red and blue dashes). They showed dimensions comparable to the corresponding inverse micelles lacking metal precursors. The huge size difference between the inverse micelles formed in the presence and absence of resorcinarene amine persisted, even in the presence of metal precursors. The DLS analysis of the inverse micelles containing resorcinarene amine and metal precursors also showed a much smaller species \( \sim 2 \) – \( 3 \) nm (Figure 32). The smaller peak could be either due to the presence of a much smaller oligomeric species or artifacts\(^{294}\) from DLS analysis. These DLS data and the results of the reversed Brust-Schiffrin syntheses strongly suggest the incorporation of the resorcinarene amine surfactant in the TOABr derived inverse micelles, where the nanoparticles are being formed.

Given the lack of solubility of resorcinarene amine (or its hydrochloride salt) in water, we expect it to be on the surface of the inverse micelle with the amine headgroups pointed towards the water pool, rather than being solubilized inside the micelle. Although these results appear to contradict the recent work of Tong and coworkers concerning the role of the surfactant,\(^ {97} \) it agrees with Pileni and coworkers,\(^ {38} \) who have invoked the involvement of both the surfactant and the TOABr in the inverse micelle formation.
Figure 3.2. DLS analysis of inverse micelles formed from TOABr + resorcinarene amine (blue trace) and TOABr (red trace) in the absence of metal salts and TOABr + resorcinarene amine (blue dash) and TOABr (red dash) in chloroform in the presence of Pd and Pt salts.
Figure 33. UV-vis spectra of (a) Pd and Pt salts in water, (b) Pd and Pt salts in inverse micelles formed by TOABr and resorcinarene amine, (c) Pd and Pt salts in inverse micelles formed by TOABr, and (d) resorcinarene amine in chloroform.

The interaction of the phase-transferred metal salts with the inverse micelles was probed by UV-vis spectroscopy (Figure 33). The band observed ~ 259 nm for the aqueous mixture of Pt and Pd metal salts was red shifted in the absence of inverse micelles (Figure 33a). The $\lambda_{\text{max}}$ of the metal salts in the presence of inverse micelles containing resorcinarene amine (Figure 33b) showed a lesser red shift (~ 266 nm) when compared to the inverse micelles formed exclusively with TOABr (~ 272 nm) (Figure 33c). Visually while the former appeared yellow, the latter appeared reddish brown. The UV-vis data suggests that the resorcinarene amine present in the inverse
micelle interacts with the metal salts even prior to their reduction. This observation is unlikely to be due to the mere presence of resorcinarene amine, as its UV-vis spectrum showed a more red shifted peak ($\lambda_{\text{max}} = 280$ nm) and much weaker absorbance.

Figure 34. $^1$H-NMR spectra of (a) inverse micelles formed by TOABr and resorcinarene amine in the absence of metal salts and presence of (b) both Pd and Pt salts, (c) Pt, and (d) Pd salts.
To gain a better understanding of the complexation of the metal salts to the resorcinarene amine surfactant, \( ^1\)H NMR spectroscopic analysis was carried out (Figure 34). In the presence of both Pt and Pd salts, the peaks from the resorcinarene amine were substantially broadened or shifted, such as O–CH\(_2\)–O protons (5.92 and 4.35 ppm), CH protons (4.76 ppm) and N–CH\(_2\)– protons (3.6 ppm) (Figure 34b), whereas no significant shift in the resorcinarene amine peaks was observed when mixed with TOABr only (Figure 34a). This data indicates that the resorcinarene amine surfactant could be strongly complexed with the metal salts. It is worth noting that the complexation of metal salts by dendrimers has been known to result in the broadening and shift of methylene protons attached to the N.\(^{295}\) The NMR studies in the presence of Pt or Pd salts showed that the resorcinarene amine was strongly complexed with Pd (Figure 34d) and not Pt (Figure 34c). Complexation has been shown to alter the redox potential of the metal ions and vary the reduction rate of the metal precursor.\(^{296}\) This work suggests that the complexation of the Pd with the resorcinarene amine surfactant occurs prior to the reduction step which could alter the reduction rate of the Pd precursors.

Based on these experiments and relevant literature, we believe that the preferential formation of Pt rich bipodal nanoparticles and Pd rich spherical nanoparticles in Brust-Schiffarin synthesis could be due to the differential stabilization of a) Pt and Pd precursors and b) the nuclei formed, both by the resorcinarene amine surfactant. The nucleation stage and in particular the nuclei formed initially have a profound influence on the final shape\(^{297}\) and composition of the nanoparticles. Once the nuclei are formed they will be capped with organic surfactants. Studies have shown the binding of amine functional groups to both Pt and Pd metal surfaces\(^{298}\) and nanoparticles.\(^{38,270}\) However, the stabilization of Pt and Pd metal surfaces by amine surfactant could differ due to potential differences in interaction energies between the ligand and metal surfaces and the adsorption geometries.\(^{299}\) It is worth noting that the selective stabilization of Pt metal by amine surfactant has been invoked in the formation of AuPt bimetallic nanowires.\(^{300}\)

3. 3. Suzuki-coupling using PdPt bimetallic nanoparticles

The V-shaped PdPt bimetallic nanoparticles prepared in the presence of resorcinarene amine surfactant were tested as catalysts in the Suzuki cross-coupling reaction. This reaction between aryl boron derivatives and aryl halides is a versatile and powerful carbon-carbon bond forming
Though usually accomplished by organopalladium complexes, it has also been catalyzed by a variety of metal nanoparticles.\textsuperscript{82,302,303} In the case of Pt nanoparticles, their shape plays a crucial role in determining their catalytic activity in Suzuki reactions.\textsuperscript{64} In contrast to tetraoctylammonium formate stabilized spherical Pt nanoparticles which are catalytically inactive,\textsuperscript{82} PVP stabilized tetrahedral Pt nanoparticles have yielded a modest 14\% conversion.\textsuperscript{304} On the other hand, Pd is a very effective metal in mediating Suzuki catalysis.\textsuperscript{302}

The yields of the biphenyl obtained in the presence of bimetallic and monometallic nanoparticle catalysts are summarized in Table 2. While as-prepared bimetallic nanoparticles produced 72\% of biphenyl, in the case of purified nanoparticles 49\% were obtained. It is worth noting that the PdPt bimetallic nanoparticle dispersions were visibly stable (with no precipitation) after the catalysis, even under rigorous reaction conditions (> 110 °C for 48 h). The TEM analysis of the PdPt bimetallic nanoparticles after the catalysis showed that they were intact but aggregated (Figure 35). This observation is remarkable as El-Sayed and coworkers have shown that a majority of the tetrahedral Pt nanoparticles undergo a shape change to spherical nanoparticles after just 24 h (2 x 12 h cycles of catalysis) of reflux under similar reaction conditions.\textsuperscript{304} Note that these catalysts contain both Pt rich V-shaped PdPt bimetallic nanoparticles and Pd rich PdPt spherical bimetallic nanoparticles.

We also investigated the efficiency of monometallic Pd and Pt nanoparticles prepared in the presence of resorcinarene amine surfactant under these reaction conditions (Table 2). While 59\% of biphenyl was obtained with Pd monometallic nanoparticle catalysts, < 2\% conversion was observed in the presence of monometallic Pt nanoparticles. Our observation is remarkable, as typically PdPt bimetallic nanoparticles are less effective than Pd nanoparticles in mediating Suzuki reactions.
Table 2. Summary of the yields of biphenyl in Suzuki coupling reaction using various bi- and mono-metalllic nanoparticle catalysts.

![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>Nanoparticle catalysts</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdPt (as prepared)</td>
<td>72</td>
</tr>
<tr>
<td>PdPt (purified)</td>
<td>49</td>
</tr>
<tr>
<td>Pd (as prepared)</td>
<td>59</td>
</tr>
<tr>
<td>Pt (as prepared)</td>
<td>&lt; 2</td>
</tr>
</tbody>
</table>

![TEM images](image)

Figure 35. TEM images of bimetallic PdPt nanoparticle catalysts after Suzuki coupling reaction.
4. Summary

The Brust-Schiffrin reduction of Pt and Pd precursors in the presence of a resorcinarene amine surfactant led to the formation of anisotropic, Pt rich, crystalline PdPt nanoparticles dominantly of a bipodal V-shape or variants on the V-shape and Pd rich spherical PdPt nanoparticles. The percentage of V-shaped and one-arm bent V shaped PdPt nanoparticles could be increased by a simple precipitation-redispersion approach. The effect of reaction parameters, such as resorcinarene amine surfactant, metal precursors, temperature, solvents, residual acid and reaction medium, have been investigated. These results show that the resorcinarene amine surfactant and water play a crucial role in the formation of the V-shaped PdPt nanoparticles. The DLS analysis of the species obtained in the presence of both resorcinarene amine and TOABr, and TOABr alone were different. In addition to UV-vis study, NMR analysis unambiguously showed the complexation of the Pd salts by resorcinarene amine surfactants. These results strongly suggest the incorporation of the resorcinarene amine in the inverse micelles formed by TOABr. Remarkably, the studies show that the composition of the V-shaped PdPt nanoparticles could be varied substantially by varying the order of addition of resorcinarene amine surfactant and sodium borohydride, and the delay time between the additions, or other reaction conditions. These anisotropic PdPt bimetallic nanoparticles prepared in the presence of resorcinarene amine surfactant show better catalytic activity than monometallic Pd nanoparticles in Suzuki cross-coupling reactions.

The Brust-Schiffrin reduction of Pt and Pd precursors in the presence of a resorcinarene benzylthiol surfactant led to the formation of anisotropic PdPt nanoparticles. These anisotropic nanoparticles were substantially richer in Pt than those obtained in the presence of resorcinarene amine surfactant under similar conditions. This work shows that the headgroup of the resorcinarene surfactant can indeed alter the composition of the bimetallic nanoparticles formed.
CHAPTER 4

DISPERSION STABILIZATION OF METAL NANOPARTICLES BY IONIC RESORCINARENE SURFACTANTS

1. Introduction

Metallic nanoparticles have attracted intense interest due to their unique size-and shape-dependent physical and optical properties. In particular, gold nanoparticles are of great interest due to their potential applications ranging from catalysis to biomedicine.

Synthetic protocols have been developed for the direct synthesis of metal nanoparticles in either water/polar solvents or non-polar organic solvents. In 1857, Faraday prepared gold colloids for the first time by the chemical reduction of Au(III) ions in the presence of phosphorous in water. In 1951, Turkevich et al. reported the synthesis of Au nanoparticles using citrate reduction of gold salts in the aqueous phase with an average size range of 20 ± 1.25 nm at 100°C. Frens refined this citrate reduction method in 1973 and obtained Au nanoparticles with various sizes between 16 and 147 nm. The size was controlled by changing the ratio of HAuCl₄ to the sodium citrate solutions. Another attractive preparation method of gold nanoparticles is the two-phase (toluene/water) reaction using a phase transfer reagent, which was first developed by Brust and co-workers. This method typically yields organic surfactant functionalized nominally spherical nanoparticles in the size domain of 1 – 6 nm dispersible in organic solvents.

The synthetic approaches leading to the dispersion of nanoparticles in either aqueous or organic medium have their own advantages and disadvantages. For instance, water-based gold nanoparticle synthesis offers a simple/easy synthetic method and no additional stabilization is needed to prevent nanoparticle agglomeration. In addition, the formation of bioconjugates with gold nanoparticles can be accomplished in water-based synthesis. On the other hand, the synthesis of gold nanoparticles in organic solvent allows better size control of the nanoparticles and monodispersity. The other advantage of the synthesis of gold nanoparticles in organic
Most studies focus on the phase transfer of particles from aqueous to organic media.\textsuperscript{103,312} However, Gittins and Caruso have reported the phase transfer of nanoparticles from organic solvent to the aqueous phase.\textsuperscript{316,317} They showed the spontaneous phase transfer of tetraoctylammonium bromide (TOABr) stabilized metal (Au and Pd) nanoparticles synthesized in toluene into water in the presence of 4-dimethylaminopyridine (DMAP).\textsuperscript{316} There is an electrostatic attraction between the negatively charged endocyclic nitrogen atoms and the positively charged metal surface, causing exocyclic nitrogen atoms to be positively charged. Thereby, the nanoparticles could be stabilized by DMAP and phase transferred into water. In another report, they showed the phase transfer of TOABr stabilized metal (Au, Ag, Pt, and Pd) nanoparticles from toluene into water using 11-mercaptoundecanoic acid.\textsuperscript{317} This approach employs a ligand exchange approach to transfer the nanoparticles into the aqueous phase via metal–thiolate bond formation.\textsuperscript{317}

A variety of surfactants and methods have been employed for the extraction of gold nanoparticles into organic solvents.\textsuperscript{103,312} The phase transfer of nanoparticles into organic solvents by small molecule ligands have been typically limited to smaller nanoparticles.\textsuperscript{193,318} For example, chemisorptive surfactants such as alkanethiols have been used to stabilize small gold nanoparticles (dimensions <10 nm) against aggregation in hydrocarbon solutions.\textsuperscript{319} However, alkanethiol stabilized nanoparticles (larger than 10 nm in diameter) often show poor long-term stability and precipitate at ambient temperatures, as the steric repulsive forces provided by such surfactants are overwhelmed by the increased van der Waals forces between larger nanoparticles in organic media.\textsuperscript{193,318} Ligand exchange\textsuperscript{318} and covalent chemical functionalization\textsuperscript{320} have also been used to phase transfer larger gold nanoparticles into the organic phase. The binding of the surfactant to the nanoparticle surfaces plays an important role in the stability of the nanoparticle dispersions and their subsequent transfer. For the phase transfer protocols, the binding affinity of
the incoming ligand with the nanoparticle surface must be equal or higher than that of the intrinsic ligand in the parent medium. These approaches often result in permanent surface modification of nanoparticles with implications for their applications. Ligands with strongly binding surface functionalities have been known to reduce catalytic activity. Thus, there is a need to develop new ligands which can stabilize metal nanoparticles effectively without compromising their catalytic activity.

Ionic interactions have also been exploited, albeit limitedly, to phase transfer gold nanoparticles from the aqueous to organic phase or vice versa. For example, citrate stabilized gold nanoparticles have been phase transferred from aqueous phase into organic solvents using ionic surfactants such as sodium oleate, tetraoctylammonium bromide, and dimethyldioctadecylammonium bromide. These approaches work by the ion-pairing of surfactant ions with surface bound counterions of the nanoparticles leading to an electrostatic interaction. Despite these advances, the current phase-transfer protocols still have severe drawbacks such as incomplete extractions, longer durations, and numerous steps, including solvent exchanges, poor reproducibility, and lack of information on long-term stability. Thus, there is a need to develop efficient methods for the phase transfer of nanoparticles.

Direct synthesis of nanoparticles in the presence of ionic surfactants as stabilizers in the organic phase has also been developed. Ionic quaternary ammonium surfactants such as tetraoctylammonium bromide (TOABr), cetyltrimethylammonium bromide (CTAB), etc., can provide electrosteric stabilization to protect nanoparticles from aggregation. Fink and coworkers synthesized gold nanoparticles in the exclusive presence of TOABr under Brust-Schiffrin conditions described earlier, where TOABr acts as both a phase-transfer agent and a stabilizer. They obtained TOABr capped gold nanoparticles with a size range from 3 to 5 nm in toluene. Wang and coworkers have synthesized gold nanoparticles in the presence of CTAB under two-phase (toluene/water) reaction conditions. They employed CTAB as both a phase-transfer agent and a stabilizer without using any additional surfactant. The gold salts phase transferred by CTAB were reduced by sodium borohydride, yielding CTAB capped gold nanoparticles in toluene with an average size <3 nm. The Br⁻ of quaternary ammonium salts are absorbed on the metal surfaces. The Br⁻ chemisorbed on the metal surfaces forms an ion pair.
with the cationic quaternary ammonium group, leading to the formation of a double-layer which helps stabilize the nanoparticles.\textsuperscript{327,328} When compared to thiols, these quaternary ammonium salts are weakly bound to the surface of nanoparticles.\textsuperscript{327,328} The nanoparticles stabilized by TOABr alone have poor long-term dispersion stability.\textsuperscript{329} In addition, the removal of solvents from the colloidal solution containing TOABr stabilized Au nanoparticles leads to sintering of the particles, and results in insoluble materials.\textsuperscript{330}

In order to improve the dispersion stability of TOABr stabilized Au nanoparticles, various anion treatments (using Na$_2$S$_2$O$_3$, Na$_2$S, NaNO$_3$, and NaH$_2$PO$_4$) have been developed.\textsuperscript{329,330} Shon and coworkers explained that weak interactions between the bromide anions and the Au surfaces caused a poor long-term stability.\textsuperscript{329,330} They showed Au nanoparticles synthesized in the presence of tetraoctylammonium thiosulfate showed improved chemical and thermal stabilities.\textsuperscript{329} Beyond direct synthesis, they also showed that when tetraoctylammonium bromide stabilized Au nanoparticles in toluene were mixed with aqueous solutions containing excess anions such as Na$_2$S$_2$O$_3$, Na$_2$S, NaNO$_3$, and NaH$_2$PO$_4$, the stability of the Au nanoparticles substantially improved.\textsuperscript{330}

Among various surfactants employed for the stabilization of nanoparticles, macrocyclic and multidentate surfactants are appealing as they can potentially lead to enhanced stability, permit supramolecular interactions, and be advantageous in catalytic applications.\textsuperscript{21,114,153,167,191,193,331-336} Wei and coworkers showed that citrate stabilized gold nanoparticles can be extracted into organic solvents by two resorcinarene-derived surfactants with thiol headgroups, such as tetrabenzylthiol resorcinarene and tetaarylthiol resorcinarene.\textsuperscript{191,331} In particular, tetrabenzylthiol resorcinarene was very effective in the phase transfer of gold nanoparticles of a wide range of sizes up to 87 nm. Also, ~19 nm Au nanoparticles phase-transferred using tetrabenzylthiol resorcinarene were found to be exceptionally stable dispersions in organic medium. Their work showed that the extraction and dispersion stability of nanoparticles in nonpolar solvents was strongly dependent on the nature of the resorcinarene headgroup.\textsuperscript{191,331} Resorcinarenes have two remarkable advantages that contribute to their superior stabilization performance: (1) the robust, multidentate binding of macrocyclic headgroups onto the nanoparticle surface and (2) the well-separated, great mobility of hydrocarbon chains, which ensures the high degree of configurational freedom per chain in the surfactant layer. This feature
offers effective entropic steric repulsion no matter how densely the resorcinarene headgroups are packed on the nanoparticle surface. Chen and coworkers showed that citrate stabilized nanoparticles (~12 nm in size) in the aqueous phase were transferred into the organic phase with C-undecylcalix[4]-resorcinarene (C11-resorcinarene) (see Scheme 1a in Chapter 1). This unfunctionalized C11-resorcinarene plays the role of a phase transfer and a stabilizing agent. However, the nature of the interaction between unfunctionalized resorcinarene and the metal surface is unclear.

We have developed amphiphilic resorcinarene surfactants to replace and or augment TOABr in direct synthesis of metal nanoparticles under the Brust-Schiffrin conditions and employ them in the phase transfer of the nanoparticles. In this chapter, multidentate resorcinarene ionic surfactants functionalized with tetrapyrindinium tetrabromide (7), tetrtrimethylammonium tetrabromide (8), and tetratributylammonium tetrabromide (9) (Scheme 4) were prepared and evaluated for their ability to stabilize gold nanoparticles in aqueous and organic media. The ammonium headgroups with various alkyl chains and steric requirements will interact with various anions differently and we wanted to study their influence. While tetrtrimethylammonium tetrabromide resembles CTAB, tetratributylammonium tetrabromide (9) is somewhat structurally similar to TOABr. We showed that resorcinarenes 7–9 can efficiently phase transfer citrate stabilized gold nanoparticles into organic solvents (Scheme 5) via a simple, fast, and efficient process. These cationic resorcinarenes can electrostatically complex with the negatively charged citrate stabilized nanoparticle surfaces and stabilize them via steric stabilization. We have evaluated the critical parameters controlling the extraction of the nanoparticles into the organic phase. Further, we have demonstrated that the stability under a variety of conditions of the resorcinarene passivated nanoparticles varied with the nature of the resorcinarene headgroup. In particular, gold nanoparticles stabilized by resorcinarene 7 exhibited exceptional (a) long-term dispersion stability, (b) resistance to aggregation in the presence of thiourea, and (c) processability and could be precipitated and redispersed in nonpolar solvents.

Furthermore, we successfully employed these ionic resorcinarene surfactants 7–9 in the direct synthesis of Au nanoparticles under Brust-Schiffrin conditions. We have also evaluated the effects of various resorcinarene headgroups in determining the long-term stability of such Au nanoparticles. Additionally, based on electrochemical analyses, we demonstrate that these
resorcinarene surfactants with non-interacting triflate counterions can interact with the Au surfaces, even in the absence of a bromide counterion. The nanoparticles stabilized by resorcinarene 7 were exceptionally stable, even in the presence of either cationic or anion dyes. This observation is notable as the addition of dyes to ionically stabilized nanoparticles has been known to trigger aggregation of the nanoparticles into large arrays and additionally to trigger disintegration of nanoparticles into other sizes.\textsuperscript{337,338} We also evaluated the stability of these gold nanoparticles passivated by resorcinarene 7 towards phase-transfer into aqueous medium in the presence of DMAP. We have also evaluated the ability of these ionic resorcinarene surfactants to entirely replace the TOABr in the phase-transfer and synthesis of nanoparticles.

2. Experimental Section

2.1. General Remarks

Pyridine (EMD, 99.8 %), trimethylamine (Acros Organic, 7 %, 1 M solution in THF), tributylamine (Aldrich, 98.5+ %), pyrene (Acros Organic, 98+ %), tetraoctylammonium bromide (Alfa Aesar, 98+ %), and tetrabutylammonium perchlorate (Fluka, 99+ %) were obtained from commercial sources and used as is, without further treatment. Thiourea (Acros Organic, 99 %) was recrystallized from water. The detailed preparation of resorcinarene tetrabenzyldibromo cavitand was described under the experimental section in Chapter 2. Citrate stabilized gold nanoparticles of three different sizes (18 ± 2 nm (n = 109), 23 ± 3 nm (n = 145) and 29 ± 8 nm (n = 126)) were obtained from Dr. Ramjee. Barnstead Nanopure water (18.2 MΩ•cm) was used for the synthesis of the nanoparticles. Acetonitrile was universal grade (high purity solvent, BDH) with a water content of < 0.01 %. All other organic solvents used were dried and distilled before use. All glassware used were silanized. Note that unless otherwise stated as “exclusive” or “exclusively”, all gold nanoparticles were prepared in the presence of both TOABr and resorcinarene surfactants.

2.2. Synthesis of resorcinarene tetrapyridinium tetrabromide 7

To a solution of resorcinarene tetrabenzyldibromo cavitand 3 (0.406 g, 0.326 mmol) in toluene (8 mL), pyridine (0.600 mL, 7.419 mmol) was added at 0 °C under argon atmosphere and stirred at the same temperature for 30 min, and then at room temperature for an additional 30 min. The reaction mixture was subsequently heated at 75 °C overnight. The volatiles were removed from the reaction mixture under reduced pressure and the residue obtained was azeotroped three times with toluene (8 mL) and CHCl₃ (5 mL). The crude product obtained after drying (almost quantitative recovery) was recrystallized from methanol-THF solvent system to obtain the title compound as a white solid (0.357 g, 70 % yield). IR (neat, cm⁻¹): 3132, 3018, 2927, 2854, 1632, 1479, 980. ¹H-NMR (DMSO-d₆, 400 MHz): δ 9.02 (d, J = 5.6 Hz, 8H), 8.65 (t, J = 7.6 Hz, 4H), 8.19 (t, J = 7.2 Hz, 8H), 7.79 (s, 4H), 6.35 (d, J = 8 Hz, 4H), 5.77 (s, 8H), 4.58 (t, J = 8 Hz, 4H), 4.53 (d, J = 7.6 Hz, 4H), 2.36 (m, 8H), 1.32 – 1.18 (m, 32H), 0.73 (t, J = 6.8 Hz, 12H). FTICR-ESI MS: (m/z (observed) = 439.88016; expected for (C₈₀H₉₆N₄O₈Br₄ - 3Br)³⁺ = 439.87984. 
2.3. Synthesis of resorcinarene tetratrimethylammonium tetrabromide 8

To a solution of trimethylamine (0.473 g, 8 mmol) in THF (8 mL), resorcinarene tetrabenzylation bromo cavitand 3 (0.400 g, 0.321 mmol) was added at 0 °C under argon atmosphere and stirred at the same temperature for 4 h, and then at room temperature for an additional 4 h. The volatiles were removed under reduced pressure and the residue obtained was azeotroped three times with THF (5 mL) and CHCl₃ (5 mL). After drying for a day under vacuum, the product was obtained as a white solid with almost quantitative yield. IR (neat, cm⁻¹): 3012, 2924, 2853, 1641, 1588, 1472, 966. ¹H-NMR (DMSO-d₆, 400 MHz): δ 7.93 (s, 4H), 6.25 (d, J = 8.4 Hz, 4H), 4.64 (t, J = 8 Hz, 4H), 4.26 (s, 8H), 4.07 (d, J = 7.6 Hz, 4H), 3.05 (s, 36H), 2.47 (m, 8H), 1.38 – 1.2 (m, 32H), 0.84 (t, J = 6.8 Hz, 12H). FTICR-ESI MS: m/z (observed) = 1399.69779; expected for (C₇₂H₁₁₂N₄O₈Br₄–Br)⁺ = 1399.60043.

2.4. Resorcinarene tetratributylammonium tetrabromide 9

To a solution of resorcinarene tetrabenzylation bromo cavitand 3 (0.348 g, 0.280 mmol) in THF (7 mL), tributylamine (1.640 mL, 6.884 mmol) was added at 0 °C under argon atmosphere and stirred for 30 min at the same temperature and then room temperature for another 30 min. Then, the reaction mixture was heated at 50 °C. After 2 days of heating, volatiles were removed under reduced pressure and the residue obtained was azeotroped with hexanes (2 × 5mL) and toluene (10 mL). The crude product obtained after drying (almost quantitative recovery) was recrystallized from a chloroform-diethyl ether solvent system to obtain the title compound as a white solid (0.510 g, 92 % yield). IR (neat, cm⁻¹): 2958, 2929, 2872, 1585, 1467, 970. ¹H-NMR (DMSO-d₆, 400 MHz): δ 8.01 (s, 4H), 6.18 (d, J = 8.0 Hz, 4H), 4.64 (t, J = 8 Hz, 4H), 4.26 (s, 8H), 4.17 (d, J = 7.2 Hz, 4H), 3.22 (m, 24H), 2.50 (m, 8H), 1.52 (m, 24H), 1.26 (m, 32H), 0.91 (t, J = 7.2 Hz, 36H), 0.84 (t, J = 6.4 Hz, 12H). FTICR-MS: m/z (observed) = 581.77846; expected for (C₁₀₈H₁₈₄N₄O₈Br₄–3Br)⁰⁰⁰ = 581.77715.

2.5. Phase transfer of nanoparticles

To an aqueous gold colloid (1 mL), an equal volume of a 3–4 mM solution of resorcinarenes 7–9 (~5 – 6 mg/mL) in acetonitrile was added and the mixture was vigorously agitated for a minute using a vortex mixer. To this 1 mL of toluene was then added and agitated for 30s, resulting in
the formation of a strong pink emulsion. Addition of 2 drops of concentrated HCl (~40 μL) and agitation for 10 seconds, led to the immediate clearing of the emulsion and the simultaneous transfer of gold nanoparticles into the organic phase.

2. 6. Stability test of nanoparticles in the presence of a competing agent

To a diluted dispersion of citrate stabilized 18 nm gold nanoparticles (0.5 mL) in water (2 mL), resorcinarene surfactants 7 or 8 (2.8 mg) were added and allowed to equilibrate for 2 days in the dark. The extinction spectra of these dispersions were monitored at various time periods after the addition of a thiourea solution in acetonitrile (1 mM, 5 μL).

2. 7. Synthesis of Gold nanoparticles in the exclusive presence of resorcinarene 8 surfactant

To an aqueous solution of HAuCl₄ (19.5 mg, 0.057 mmol, 2 mL), an organic solution of resorcinarene 8 (37.3 mg, 0.025 mmol) in dichloromethane (8 mL) was added and vigorously stirred for 30 min at room temperature under ambient atmosphere. Even after stirring for 30 min, the aqueous phase changed from a yellow solution to a cloudy yellowish suspension, while the organic phase changed from colorless to a reddish yellow blurry suspension. The organic phase was collected, cooled to 0 °C, and a solution of sodium borohydride (21.7 mg, 0.574 mmol) in ice cold water (2 mL) was added and stirred at the same temperature. The color of the reaction mixture transitioned from a reddish yellow suspension to dark purple within 5 min after the addition of sodium borohydride. After 15 min of stirring at room temperature, the organic layer was collected and washed with copious amounts of water (8 mL × 3).

2. 8. Synthesis of Gold nanoparticles in the exclusive presence of resorcinarene 9 surfactant

To an aqueous solution of HAuCl₄ (19.5 mg, 0.057 mmol, 2 mL), an organic solution of resorcinarene 9 (42.4 mg, 0.037 mmol) in chloroform (8 mL) was added and vigorously stirred for 30 min at room temperature under ambient atmosphere, to transfer the metal salts into the organic phase. During stirring, the color of the aqueous phase changed from yellow to colorless, while that of the organic phase changed from colorless to reddish blurry orange. The organic phase was collected, and a solution of sodium borohydride (21.9 mg, 0.579 mmol) in ice cold water (2 mL) was added. The color of the reaction mixture transitioned from reddish blurry orange to dark reddish purple immediately after the addition of sodium borohydride. After 1 h of
stirring at 0 °C, the organic layer was collected and washed with copious amounts of water (8 mL × 3).

2. 9. Synthesis of Gold nanoparticles in the presence of resorcinarene surfactants 7–9

To an aqueous solution of HAuCl₄ (19.5 mg, 0.057 mmol, 2 mL), an organic solution of tetraoctylammonium bromide (47.1 mg, 0.086 mmol) in chloroform (4 mL) was added and vigorously stirred for 30 min at room temperature under air atmosphere, to transfer the metal salts into the organic phase. During stirring, the color of the aqueous phase changed from yellow to colorless, while that of the organic phase changed from colorless to reddish orange. The organic phase was collected and stirred with resorcinarene surfactant (7: 22.4 mg, 8: 21.4 mg, and 9: 28.5 mg, 0.014 mol, respectively) in chloroform (4 mL) for 30 min at room temperature. The reaction mixture was subsequently cooled to 0 °C and a solution of sodium borohydride (21.9 mg, 0.579 mmol) in ice cold water (2 mL) was added. The color of the reaction mixture transitioned from reddish orange to dark reddish wine in the case of 7 and 9, and to dark purple in the case of 8 within 30 s after the addition of sodium borohydride. After 1 h of stirring at 0 °C, the organic layer was collected and washed with copious amounts of water (8 mL × 3).

2. 10. Synthesis of resorcinarene tetrapyridinium tetratriflate 10

To a solution of resorcinarene tetrapyridinium tetrabromide 7 (0.148 g, 0.095 mmol) in methanol (2.5 mL), a solution of silver triflate (0.109 g, 0.424 mmol) in methanol (2.5 mL) was added and stirred at 50 °C for 2 days under Ar atmosphere. After 2 days of stirring, an additional 15 mL of methanol was added and then stirred at the same temperature for an hour. The dark gray precipitate obtained during the reaction was filtered off and the filtrate was collected. The crude compound obtained after the removal of the volatiles was purified by precipitation. It was precipitated by the addition of water (~10 mL) to a concentrated solution in methanol (>2 mL). Precipitate was collected and azeotroped twice with acetonitrile (5 mL). After drying for a day under vacuum, the title compound 4 was obtained as an off-white solid (0.137 g, 79 % yield).IR (neat, cm⁻¹): 3133, 3061, 2928, 2856, 1633, 1477, 979. ¹H-NMR (DMSO-d₆, 400 MHz): δ 8.97 (d, J = 8 Hz, 8H), 8.65 (t, J = 8 Hz, 4H), 8.19 (t, J = 8 Hz, 8H), 7.73 (s, 4H), 6.32 (d, J = 8 Hz, 4H), 5.70 (s, 8H), 4.59 (t, J = 8 Hz, 4H), 4.52 (d, J = 8 Hz, 4H), 2.35 (m, 8H), 1.34 – 1.15 (m, 32H), 0.74 (t, J = 6 Hz, 12H).
2. 11. Synthesis of resorcinarene tetrtrimethylammonium tetratriflate 11

To a solution of resorcinarene tetramethylammonium tetrabromide 8 (0.142 g, 0.096 mmol) in methanol (2.5 mL), a solution of silver triflate (0.111 g, 0.431 mmol) in methanol (2.5 mL) was added and stirred at 50 °C for 2 days under Ar atmosphere. After 2 days of stirring, an additional 15 mL of methanol was added and then stirred at the same temperature for an hour. The dark gray precipitate obtained during the reaction was filtered off and the filtrate was collected. The crude compound obtained after the removal of the volatiles was purified by precipitation. It was precipitated by the addition of water (~10 mL) to a concentrated solution in methanol (>2 mL). Precipitate was collected and azeotroped twice with acetonitrile (5 mL). After drying for a day under vacuum, the title compound 5 was obtained as an off-white solid (0.100 g, 73 % yield). IR (neat, cm⁻¹): 3040, 2928, 2856, 1643, 1588, 1473, 966. ¹H-NMR (DMSO-d₆, 400 MHz): δ 7.87 (s, 4H), 6.17 (d, J = 8 Hz, 4H), 4.64 (t, J = 8 Hz, 4H), 4.18 (s, 8H), 4.08 (d, J = 8 Hz, 4H), 3.03 (s, 36H), 2.43 (m, 8H), 1.40 – 1.24 (m, 32H), 0.85 (t, J = 6 Hz, 12H).

2. 12. Synthesis of resorcinarene tetratributylammonium tetratriflate 12

To a solution of resorcinarene tetratributylammonium tetrabromide 9 (0.126 g, 0.063 mmol) in methanol (2.5 mL), a solution of silver triflate (0.073 g, 0.286 mmol) in methanol (2.5 mL) was added and stirred at 50 °C for 2 days under Ar atmosphere. After 2 days of stirring, an additional 15 mL of methanol was added and then stirred at the same temperature for an hour. The dark gray precipitate obtained during the reaction was filtered off and the filtrate was collected. The crude compound obtained after the removal of volatiles was dissolved in dichloromethane (10 mL) and washed with water (10 mL) three times. The title product obtained after the removal of volatiles was azeotroped with dichloromethane (2 x 5 mL) and chloroform (5 mL). After drying for a day under vacuum, the title compound 6 was obtained as an off-white solid (0.114 g, 80 % yield). IR (neat, cm⁻¹): 2961, 29230, 2874, 1587, 1469, 971. ¹H-NMR (DMSO-d₆, 400 MHz): δ 7.90 (s, 4H), 6.12 (d, J = 8.0 Hz, 4H), 4.65 (t, J = 8 Hz, 4H), 4.20 (s, 8H), 4.17 (d, J = 8 Hz, 4H), 3.21 (m, 24H), 2.43 (m, 8H), 1.52 (m, 24H), 1.26 (m, 32H), 0.93 (t, J = 8 Hz, 36H), 0.86 (t, J = 8 Hz, 12H).
2.13. Fluorescence measurements

To probe the existence of a critical micellar or aggregation concentration, fluorescence emission spectra of an aqueous solution of pyrene (1.9 µM) was recorded by exciting it at 336 nm (2.5 nm slit) and the emission was monitored from 350 to 420 nm (2.5 nm slit). Resorcinarene surfactant (7: 7.8 mg and 8: 7.4 mg, 2 mM) was dissolved in the aqueous 1.9 µM pyrene solution (2.5 mL). The resulting resorcinarene surfactant stock solution (2 mM) was diluted with aliquots of aqueous pyrene (1.9 µM) solution to obtain various concentrations of resorcinarene surfactant and their fluorescence spectra were recorded and the $I_3/I_1$ ratio monitored at 384 and 373 nm, respectively.

2.14. Electrochemical measurements

Cyclic voltammetry was carried out using a BASi epsilon potentiostat and the data was collected using epsilon software. For these studies, 1 mM solutions of resorcinarene quaternary ammonium triflate surfactants in acetonitrile (5 mL) in the presence of 0.10 M tetrabutylammonium perchlorate as electrolyte were employed. These studies were carried out in a single compartment cell containing 2 mm Au working electrode, coiled Pt wire counter electrode and Ag/AgCl electrode as reference electrode. The Au working electrode was polished with 0.25 µm diamond paste, rinsed with copious amounts of water and sonicated for at least 5 min in water, then washed with acetonitrile prior to electrochemical studies. The coiled Pt wire was flame-annealed using a Bunsen burner and then rinsed with copious amounts of water and subsequently acetonitrile. The solutions were deaerated by purging with argon for at least 5 min prior to the electrochemical experiment. All electrochemical experiments were conducted under a gentle flow of argon.

2.15. Titration experiments

20 µM stock solutions of rhodamine 6G and crystal violet were prepared by dissolving a known mass of solid dye in chloroform (3 mL). In the case of Brilliant Blue G, we attempted to dissolve 2.6 mg of brilliant blue G in 15 mL of chloroform (203 µM stock solution). There were substantial amounts of insoluble material. The insoluble material was filtered off and the filtrate was collected and used as such for titration experiments. As prepared gold nanoparticle
dispersions (0.1 mL) were diluted with chloroform (2.9 mL), aliquots of dye solution (in 0.25 mL increments up to a total of 3 mL) were added, mixed for 1 min, and their extinction spectra recorded. The UV-vis spectra of gold nanoparticle dispersions and dye solutions were also recorded separately. The UV-vis spectra was recorded after the addition of each aliquot.

2. 16. Inverse extraction of gold nanoparticles into aqueous phase

Excess resorcinarene 7 in a gold nanoparticle dispersion in chloroform were removed by washing twice with water. To these gold nanoparticle dispersions in chloroform (1 mL), an equal volume of an aqueous solution of 4-dimethylaminopyridine (DMAP) (25 mM) was added and the mixture was vigorously agitated for a minute using a vortex mixer. While the organic phase was clear and colorless indicating the transfer of gold nanoparticles, the aqueous phase showed a pink emulsion. The emulsion cleared slowly and eventually gold nanoparticles were present either in the aqueous phase or interface.

2. 17. Instrumentation

$^1$H NMR spectra were obtained using a Varian Oxford 400 MHz and a Bruker Ascend™ 400 MHz instrument. Infrared spectral analysis of solution drop-cast samples was carried out in a Thermo Electron Nicolet 370 DTGS spectrophotometer. Mass spectral analysis was carried out in a Bruker 12 T APEX-Qe FTICR-ESI MS equipped with an Apollo II ion source in a positive electrospray ionization mode. UV–vis spectra were obtained in a Cary-5000 UV–vis–NIR spectrophotometer. Fluorescence spectra were recorded with an excitation and emission slit width of 2.5 nm on a Cary Eclipse Fluorescence spectrophotometer. TEM analyses were performed using a JEOL JEM-2100F field emission microscope operating at 200 kV equipped with a Gatan SC1000 ORIUS CCD camera (11 megapixel), and EDS was recorded with the attached Oxford INCAx-sight EDS detector. TEM samples were prepared by drop-casting nanoparticle dispersions on a Formvar carbon film coated copper grid. Refractive indices of resorcinarenes were measured using a Milton Roy tabletop refractometer (Abbe 3L) at 20 °C.
3. Results and Discussion

3.1. Extraction of gold nanoparticles

Resorcinarene quaternary ammonium surfactants 7–9 were prepared by the reaction of a resorcinarene tetrabenzylbromo cavitand with the corresponding amines (Scheme 4). Their synthesis and characterization details were described under the experimental section. The phase transfer of citrate stabilized gold nanoparticles into the organic phase using ionic resorcinarene surfactants was accomplished by a simple process, which can be completed within a few minutes and monitored visually. Resorcinarenes 7–9 were all effective in extracting 18 nm gold nanoparticles (Figure 36) into a toluene–acetonitrile solvent system, but there were subtle differences depending on the nature of the resorcinarene headgroup (Scheme 5). While resorcinarene 8 could completely extract gold nanoparticles into the organic phase, in the case of resorcinarene 7, some minimal amount of nanoparticles remained in the interface. In the case of resorcinarene 9 with bulkier tributylammonium groups, a significant amount of dark blue precipitate was observed along the walls of the test tube. However, the amount of precipitate varied with batches (Figure 37). The phase-transfer of gold nanoparticles into toluene-acetonitrile by resorcinarene surfactants is remarkable as resorcinarene 7–9 are insoluble in toluene and resorcinarene 7 and 8 have limited solubility in acetonitrile. On the other hand, resorcinarenes 7 and 8 are completely soluble in either water or a water/acetonitrile mixture, and resorcinarene 9 is soluble in acetonitrile.
Scheme 5. Phase transfer of gold nanoparticles by resorcinarene surfactants. The photographs show extracted 18 nm nanoparticles.

Figure 36. TEM image (scale bar = 100 nm) of 18 nm citrate stabilized gold nanoparticles.
Immediately after the addition of resorcinarene 7 in acetonitrile, the nanoparticle dispersions which were initially pink became slightly purple (Scheme 5). The UV−vis spectra exhibited a red-shift (544 nm) and a broadening of the localized surface plasmon resonance (LSPR) at this stage (ii, Figure 38a) when compared to citrate stabilized gold nanoparticles in water (i, Figure 38a) with an extinction maxima of 518 nm. The red-shift is indicative of the flocculation of gold nanoparticles, and we attribute it to the hydrophobization and subsequent flocculation of the nanoparticles in the water−acetonitrile mixture. This flocculation was temporary as the nanoparticles extracted into the toluene−acetonitrile mixture were again pink in color and showed a much narrower LSPR (iii, Figure 38a). The optical extinction spectrum of gold nanoparticles extracted by resorcinarenes 7–9 showed that the plasmon resonance peak for all three of them were slightly red-shifted when compared to the aqueous citrate stabilized gold nanoparticles (Figure 38b, solid lines). While nanoparticles extracted by resorcinarenes 7 had an extinction maxima of 530 nm, the nanoparticles extracted by resorcinarene 8 and 9 had an extinction maxima of 528 nm. During the phase transfer, both the dispersing medium and the surfactant around the gold nanoparticles are changed, and they are both known to influence the LSPR of nanoparticles. To delineate their influence, we recorded the UV−vis spectra of...
gold nanoparticles equilibrated with aqueous solutions of resorcinarenes 7–9 (Figure 38c) for 2 days. The extinction maxima of these nanoparticle dispersions in water were also red-shifted but to a lesser extent when compared to those extracted into organic phases. While nanoparticles dispersed in water in the presence of resorcinarene 7 or 8 showed an extinction maxima of 526 nm, those in the presence of resorcinarene 9 had an extinction maxima of 525 nm. Interestingly, we did not observe any broadening of the plasmon peak of the nanoparticles dispersed in water (Figure 38c) in the presence of resorcinarenes 7–9, similar to those observed in the water–acetonitrile mixture (ii, Figure 38a). We attribute the former to the interdigitation of resorcinarenes. Interdigitation is the tail-to-tail packing of resorcinarene molecules promoted by van der Waals interactions between alkyl chains, and this has been proven experimentally via crystal structure determination. Interdigitation of unfunctionalized resorcinarenes has also been demonstrated on gold surfaces, where multilayers are formed via tail-to-tail and head-to-head stacking of resorcinarenes. From these experiments, it appears that the mere addition of resorcinarenes 7–9 to nanoparticles in water contributes a 7–8 nm red-shift of the plasmon band, while further switch of the solvent to toluene-acetonitrile contributes a relatively smaller 2–4 nm red-shift.

The UV-vis spectra of the aqueous phases after the extraction (Figure 38b, dotted lines) were almost featureless in the visible region and did not show the plasmon peak characteristic of gold nanoparticles. The refractive indices of resorcinarenes 7–9 measured at 589 nm and 20 °C were 1.5207, 1.5102, and 1.5002, respectively. Given the almost identical refractive indices of resorcinarenes 7–9, the UV-vis spectra of the nanoparticles extracted into the organic phase (Figure 38b, solid lines) also provide quantitative information on the extraction efficiency of these surfactants. Since the aqueous phase did not show any optical extinction, there were no remaining nanoparticles in the aqueous phase after extractions (Figure 38b). On the basis of the absorbance values, we estimate the amount of gold nanoparticles extracted by resorcinarene 7 and 9 as 95% and 69%, respectively, when compared to resorcinarene 9 which extracts almost completely.
Figure 38. (a) UV-vis spectra of citrate stabilized gold nanoparticles (18 nm) (i) in water (ii) with resorcinarene 7 in water-acetonitrile mixture and (iii) extracted by resorcinarene 7 in toluene-acetonitrile mixture. (b) UV-vis spectra of diluted dispersions of gold nanoparticles in toluene-acetonitrile mixture (solid lines) extracted by resorcinarenes 7 (red), 8 (blue) and 9 (green) and the undiluted aqueous phase remaining after extractions (dotted lines). (c) UV-vis spectra of aqueous dispersions of gold nanoparticles in the presence of various resorcinarenes.
The transmission electron microscopic (TEM) analysis (Figure 39a and 39c) of the nanoparticles extracted by resorcinarenes 7–9 showed that the nanoparticles were well dispersed without any aggregation, and further their size and polydispersity were comparable to those of the parent nanoparticles dispersed in water (Figure 36). Notably, energy dispersive spectroscopy (EDS) analysis (Figure 39d) of the nanoparticles extracted by resorcinarene 8 showed the presence of Au, C, and O in addition to Cu from the grid and not Cl or Br.

Figure 39. TEM analysis of gold nanoparticles (18 nm) extracted by resorcinarene (a) 7 (b) 8 and (c) 9 and (d) EDS analysis of (b).
The gold nanoparticle dispersions (1 mL) extracted by surfactants 7 and 8 could be precipitated by the addition of excess methanol (10 mL) and isolated after centrifugation for 20 min at 10K rpm. Consistent with literature reports,\textsuperscript{191} though most of the nanoparticles could be precipitated, occasionally miniscule amounts of nanoparticles were lost in the supernatant during centrifugation. The material recovered after the evaporation of the supernatant obtained from the first precipitation cycle was less than approximately 5\% of the mass of added resorcinarene surfactants. We observed that most of the added resorcinarenes remained in the aqueous phase after the extraction. In the case of 4 mL scale extractions, 18.9 mg of tetrapyridinium surfactant 7 (out of 22.5 mg added) and 19.6 mg of tetratrimethylammonium surfactant 8 (out of 22.4 mg added) were recovered from the aqueous phases.
Figure 40. FT-IR spectra of resorcinarenes 7 (a) and 8 (b) and the compounds recovered from the aqueous (aq.) layer after the extraction of the nanoparticles into the organic phase. Note that the peak marked with * around ~1720 cm\(^{-1}\) observed in the recovered compounds could be from the protonation of citrate.
The IR spectra of the recovered compounds (Figure 40) matched well with the corresponding resorcinarenes 7 or 8. Twice precipitated nanoparticles could be completely redispersed in chloroform without any visible aggregation (Figure 41). This indicated that the gold nanoparticles were still coated with resorcinarene surfactants even after twice precipitation.

However, the UV–vis spectra of such redispersed nanoparticles (Figure 42) showed that the plasmon peak was somewhat broadened when compared to the parent nanoparticles, suggesting some aggregation. The IR spectrum of twice precipitated nanoparticles was different when compared to resorcinarene 8, and bands at ~ 3041, 1464, and 968 cm\(^{-1}\) were noticeably attenuated for the nanoparticles (Figure 43). The attenuation has been attributed to the complexation of the citrate on the nanoparticles with the ammonium surfactant.\(^{323}\) Further, a
binary complex from flexible calixarene based imidazolium salt has also been shown to bind citrate anion.\textsuperscript{342}
Figure 42. UV-vis spectra of nanoparticles extracted into toluene-acetonitrile mixture by resorcinarene 7 (a) and 8 (b) and the same after two rounds of precipitation and redispersion in chloroform.
3. 2. Factors influencing the extraction of nanoparticles

To probe the importance of multidentate interactions, we replaced resorcinarenes with CTAB (14.8 mM). Immediately after the addition of hydrochloric acid, the gold nanoparticles were completely destroyed (Figure 44a). In general, surfactants with longer chain lengths have been more effective in the phase transfer of gold nanoparticles. The fact that CTAB is unable to extract and or stabilize nanoparticles despite its much longer (hexadecyl) alkyl chain clearly shows the importance of multidentate interactions of resorcinarenes 7–9 in the above extraction process.

We evaluated the role of several other parameters in the extraction process using resorcinarene 8 as it typically leads to the complete extraction of nanoparticles into the organic phase. With a
lesser amount of resorcinarene 8 (0.81 mM instead of 4 mM), gold nanoparticles could only be extracted partially into the organic phase with some remaining in the interface (Figure 44b). Consistent with literature,326,344 hydrochloric acid is required for the effective phase transfer of the nanoparticles. Though the precise role of HCl in phase transfer is still unclear, it is believed to neutralize surface charges on nanoparticles345 and in some instances decompose borohydride103 on nanoparticle surfaces and thereby facilitate the adsorption of the added surfactants to the nanoparticle surfaces. When HCl was replaced with other weaker organic acids such as acetic acid, only miniscule amounts of gold nanoparticles were extracted (Figure 44c). The cosolvent acetonitrile also played a major role in the extraction process. In the absence of acetonitrile, i.e., when resorcinarene 8 was dissolved in water and added to an aqueous colloidal dispersion of gold nanoparticles, the emulsion resulting after the addition of toluene could not be broken even after the addition of concentrated HCl. The emulsion took 2 weeks to partially clear, and nanoparticles were phase transferred into an emulsified organic phase (Figure 44d). Yang and co-workers346 have similarly observed the formation of a milky emulsion in the absence of a cosolvent, and in their experiments, nanoparticles were not transferred into the organic phase. They concluded that the cosolvent increases the interfacial contact between citrate stabilized nanoparticles and the surfactant, thereby facilitating the phase transfer. Cosolvents like tetrahydrofuran14 and ethanol346 have been shown to be critical in the extraction and stability of phase transferred nanoparticles. The acetonitrile and toluene used in this extraction process could be readily changed to other solvent pairs. For example, the surfactant could be dissolved in methanol and the nanoparticles could be extracted using chloroform (Figure 44e).

In the literature, quaternary ammonium salts have been shown to be unsuccessful in breaching the 10 nm324 or 20 nm323 size limit for phase transfer of nanoparticles into organic solvents.
Figure 44. Extraction experiments carried out with 18 nm gold nanoparticles in the presence of (a) CTAB in toluene-acetonitrile (b) reduced concentration of resorcinarene 8 in toluene-acetonitrile (c) resorcinarene 8 in toluene-acetonitrile in the presence of acetic acid (d) resorcinarene 8 in water-toluene system in the absence of acetonitrile and (e) resorcinarene 8 in chloroform-methanol.

Figure 45. TEM image of 23 ± 3 nm (a) and 29 ± 8 nm (b) citrate stabilized gold nanoparticles.
Figure 46. Photographs of 23 nm (a) and 29 nm (b–e) citrate stabilized nanoparticles extracted by resorcinarenes 7 (b), 8 (a and c) and 9 (d and e) into toluene-acetonitrile. In the case of 9, immediately after the completion of the phase transfer protocol (d) some nanoparticles were extracted into the organic phase, but after 16 h (e) the dispersion was not stable.

We tested the ability of resorcinarenes 7–9 in extracting larger (23 and 29 nm sized) nanoparticles (Figure 45). While resorcinarenes 7 and 8 were effective in extracting most of the nanoparticles into the organic phase (Figure 46a–c), in the case of resorcinarene 9, nanoparticles were only partially extracted (Figure 46d). Also, varying amounts of nanoparticles remained in the interface. While nanoparticles extracted by 7 and 8 were visually stable for months (Figure 46a–c), the nanoparticles extracted by 9 (Figure 46d) were not even stable for 16 h (Figure 46e). In some instances with larger nanoparticles, our experiments using resorcinarene 9 led to the destruction of the nanoparticles even during extraction. The TEM analyses of 29 nm nanoparticles extracted by resorcinarenes 7–9 are provided in Figure 47a–c. The UV-vis spectra of these nanoparticles (Figure 47d) showed that the extinction maxima was slightly red-shifted (~ 535 nm) when compared to the smaller 18 nm particles (Figure 38b).
Figure 47. TEM analysis of gold nanoparticles (29 nm) extracted by resorcinarene (a) 7 (b) 8 and (c) 9 and (d) UV-vis spectra of 29 nm nanoparticles extracted in to toluene-acetonitrile by resorcinarene surfactants.

3. 3. Surfactant headgroup dependent stabilization of nanoparticles

To systematically probe the differences, if any, between the 18 nm gold nanoparticles stabilized by various resorcinarenes, we monitored their long-term dispersion stability. The nanoparticles extracted by resorcinarene 7 showed excellent dispersion stability over several weeks (Figure 48 and 49a) at ambient temperature with minimum changes in extinction wavelength or intensity.
Though there were minimum changes in the extinction wavelength of the nanoparticle dispersions stabilized by resorcinarene 8, there was a significant initial drop in the absorbance (Figure 48 and 49b). After the initial drop, the dispersion remained stable over several weeks.

Figure 48. Plot of the absorbance (at $\lambda_{\text{max}}$) over time of gold nanoparticles (18 nm) extracted by resorcinarenes 7–9 in toluene-acetonitrile mixture.

The TEM analysis of both these nanoparticle dispersions showed the presence of well-dispersed individual nanoparticles even after several weeks (Figure 50). In contrast, the gold nanoparticles stabilized by resorcinarene 9 with a bulky tributylammonium headgroup were unstable. The extinction wavelength changed from 528 to 534 nm within the first 4 h and further shifted to 544
nm in 32 h, and the plasmon resonance peak was also broadened (Figure 48 and 49c). The dependence of the long-term stability of the nanoparticle dispersions on the nature of the resorcinarene headgroup could be due to differences in the interaction of resorcinarenes 7–9 with the citrate anion.
Figure 49. UV-vis spectra of gold nanoparticles (18 nm) extracted by (a) 7 (b) 8 and (c) 9 at various time periods.
We further evaluated the robustness of the multidentate resorcinarene surfactants by introducing a competing surfactant. Dispersion stability of phase-transferred nanoparticles has been shown to be influenced by competing surfactants.\cite{191,331} Recently, Rao and co-workers showed that when miniscule amounts of thiourea were added to citrate stabilized gold nanoparticles in water, it caused substantial red-shifts (from 523 to 690 nm) within a minute, and further the extent of the shift depended on the concentration of thiourea.\cite{347} They tested a variety of thiourea derivatives and concluded that the replacement of the negatively charged citrate with neutral thiourea on the nanoparticle surfaces led to the controlled aggregation of the nanoparticles. In the presence of resorcinarene 7, the extinction spectra of the nanoparticle dispersions in water did not show any

Figure 50. TEM image (scale bar = 200 nm) of 18 nm gold nanoparticles extracted by (a) 7 (~312 h) and (b) 8 (after 480 h).
significant change upon the addition of thiourea (Figure 51a). However, after several hours a very slight decrease in the absorbance was noticed. In the presence of resorcinarene 8, a very slight decrease in the absorbance and a marginal blue-shift was noticed immediately after the addition of thiourea (Figure 51b). Note that no additional peaks appeared in both these cases. Consistent with literature, a control experiment carried out in the absence of resorcinarene 7 or 8 showed that the intensity of the LSPR decreased noticeably immediately after the addition of thiourea along with the concomitant appearance of a new substantially red-shifted (> 200 nm) and much broader extinction peak (Figure 51c). We also tested the resistance of the nanoparticle dispersions in the toluene-acetonitrile mixture, and the extinction spectra of the nanoparticles extracted by 7 did not show any change after the addition of thiourea (Figure 51d). All these experiments unambiguously demonstrate the robust protection provided by resorcinarenes 7 and 8 against the irreversible flocculation of the nanoparticles in both aqueous and organic medium even under adverse conditions.
Figure 51. The effect of thiourea on the UV-vis spectra of citrate stabilized gold nanoparticles (18 nm) (a) in the presence of resorcinarene 7 in water (b) in the presence of resorcinarene 8 in water (c) in water and (d) extracted by resorcinarene 7 in toluene-acetonitrile mixture.

3. 4. Direct synthesis of Au nanoparticles

We employed a modified Brust–Schiffrin procedure for the direct synthesis of gold nanoparticles in the presence of various resorcinarene quaternary ammonium surfactants. Briefly, tetraoctylammonium stabilized gold salts in chloroform were reduced with an aqueous sodium borohydride solution in the presence of resorcinarene quaternary ammonium surfactants 7–9 at 0 °C for 1 h. As a control, we attempted to prepare tetraoctylammonium stabilized gold
nanoparticles in the absence of resorcinarene surfactants. Our attempts to prepare gold nanoparticles in the exclusive presence of TOABr in either chloroform or related dichloromethane were unsuccessful. In the case of dichloromethane, a significant amount of precipitation was observed during the synthesis. In the case of chloroform, the nanoparticles were not even formed during reduction. Though TOABr stabilized gold nanoparticles have been successfully prepared by several groups in toluene, these experiments clearly reveal that they cannot be prepared in either chloroform or dichloromethane. This could perhaps be attributed to solvent dependent ion-pairing effects and stability issues in these solvents.

Figure 52. Normalized UV–vis spectra of gold nanoparticles prepared in the presence of resorcinarenes 7 (blue), 8 (red), and 9 (green) in chloroform.
The UV-vis spectra of the gold nanoparticles synthesized in the presence of resorcinarenes 7–9 exhibited localized surface plasmon resonance (LSPR) peaks at 525 nm, 528 nm, and 519 nm for resorcinarenes 7, 8, and 9, respectively (Figure 52). The media and surfactants surrounding the nanoparticles can indeed influence its LSPR due to their distinct refractive indices, and this has been documented in several publications.\textsuperscript{326,332} After the synthesis, the gold nanoparticles prepared in the presence of resorcinarene 8 surfactant were unstable. We observed a significant amount of gold precipitate. The extinction maxima of these gold nanoparticles was slightly red-shifted (528 nm) and broadened. Gold nanoparticles prepared in the presence of resorcinarene 7 and 9 showed good dispersion stability without any visible precipitates.

We employed TEM to analyze the morphology of the various nanoparticles, and all gold nanoparticles are well-dispersed. As shown in Figure 53a and b, gold nanoparticles prepared in the presence of resorcinarene 7 were mostly spherical in shape with an average size of 7.2 ± 2.0 nm (n = 166). Similarly gold nanoparticles prepared in the presence of resorcinarene 8 were also mostly spherical with an average size of 6.9 ± 1.6 nm (n = 169) (Figure 53c). The gold nanoparticles prepared in the presence of resorcinarene 9 were mostly spherical and polydisperse, and interestingly also showed some anisotropic triangular and rod-like nanostructures. The spherical nanoparticles obtained in this synthesis had an average dimension of 10.9 ± 3.8 nm (n = 95) (Figure 53d).
Figure 53. TEM analysis of gold nanoparticles prepared in the presence of resorcinarenes (a and b) 7, (c) 8, and (d) 9.
Figure 5. UV−vis spectra of gold nanoparticles prepared in the presence of (a) resorcinarenes 7, (b) 8, and (c) 9 over time.

We also monitored the long-term dispersion stability of these nanoparticles (Figure 5). The nanoparticles prepared in the presence of resorcinarene 7 revealed extraordinary dispersion stability (Figure 5a). As mentioned earlier, the gold nanoparticles prepared in the presence of resorcinarene 8 were most unstable and significant amount of precipitate formed during the synthesis. After removal of the precipitate, the gold nanoparticle dispersion was monitored by UV-vis spectroscopy. Interestingly, the extinction wavelength (528 nm) did not change even after ~ 145 h (Figure 5b). However, there were some batch dependent stability issues in the case
of gold nanoparticles prepared in the presence of resorcinarene 8. Another preparation showed that the absorbance of the LSPR peak in the gold nanoparticles prepared in the presence of resorcinarene 8 surfactant substantially decreased and broadened over time (Figure 55). We believe that this could be due to the varying amount of gold nanoparticle precipitation during synthesis. The gold nanoparticles prepared in the presence of resorcinarene 9 with bulky tributylammonium headgroups were unstable. The extinction wavelength shifted from 519 to 526 nm within the first 18 h and further shifted to 529 nm in 36 h. After 65 h, we observed that the plasmon resonance peak was significantly broadened (Figure 54c).

Figure 55. UV-vis spectra of gold nanoparticles prepared in the presence of resorcinarenes 8 over time.
3.5. Electrochemical measurements

Generally, it is believed that the cationic quaternary ammonium group merely stabilizes the bromide anion chemisorbed on the metal nanoparticle surface to provide electroneutrality.\textsuperscript{327,328} Burgess and coworkers have recently reported the adsorption of a quaternary ammonium cation on Au employing electrochemical methods.\textsuperscript{349-352} In the cyclic voltammetric analysis, they observed the adsorption/desorption peak of octyltrimethylammonium (OTA\textsuperscript{+}) at ~-0.55 V for an Au (111) surface\textsuperscript{351} and at ~-0.7 V for Au (100) even in the absence of a bromide counterion.\textsuperscript{352} Also, at potentials positive of the adsorption peak of OTA\textsuperscript{+} (i.e., in between -0.50 and 0.20 V), the capacitive currents were narrower than those of the electrolyte (NaF), indicating that the OTA\textsuperscript{+} was adsorbed on the Au (100) surface (in the absence of a bromide counterion).\textsuperscript{352} They also observed the co-adsorption of both quaternary ammonium (octyltrimethylammonium, OTA\textsuperscript{+}) cation and bromide (Br\textsuperscript{−}) anion on Au (111)\textsuperscript{351} and (100)\textsuperscript{352} surfaces (see Figure 1a and 1b in Chapter 1). Their electrochemical results revealed the higher bromide coverage on Au (111)\textsuperscript{351} than on Au (100)\textsuperscript{352} planes. The OTA\textsuperscript{+} isotherms showed no significant difference in the adsorbed OTA\textsuperscript{+} on Au (111)\textsuperscript{351} and Au (100)\textsuperscript{352} in the presence of bromide ions.

Prior to the electrochemical measurements, we wanted to confirm that at 2 mM concentration of the resorcinarene surfactants 7 and 8, they were indeed in true solution, as in principle they could be aggregated. For this purpose, we employed pyrene as a fluorescent probe.\textsuperscript{353-355} The fluorescence excitation of pyrene leads to the generation of five distinct vibronic bands (\(I_1 - I_5\)). While the intensity of \(I_1\) is dependent on the polarity of the medium, the intensity of \(I_3\) is largely independent of medium polarity, and thus the ratio of \(I_3/I_1\) is often used to determine the critical micellar concentration (cmc).\textsuperscript{356} The ratio of \(I_3/I_1\) increases when the pyrene migrates to the hydrophobic core of the micelle and is in an apolar environment. As shown in Figure 56, resorcinarene 8 in the aqueous pyrene solution had an \(I_3/I_1\) ratio of 0.66. This is a very similar value to the pyrene background \(I_3/I_1\) ratio of 0.61, indicating that these are indeed in true solution at this concentration. Our attempts to measure the fluorescence of pyrene in the presence of resorcinarene 7 were not successful, as pyridinium derivatives have been known to quench pyrene fluorescence.\textsuperscript{357}
Figure 56. Fluorescence spectra of (a) pyrene in water (1.9 µM) and (b) resorcinarene 8 (2 mM) in the aqueous pyrene solution.

For the electrochemical experiment, we used triflate anion as the counterion for the resorcinarene quaternary ammonium cation. As triflate ions have been known to only weakly adsorb on to
Au(111) and Au(100) surfaces, we chose them as counterions, which is similar to Burgess’s work. Resorcinarene surfactants with triflate counterions (10 – 12) (Scheme 6) were prepared by ion metathesis of the corresponding resorcinarene tetrabromide (7 – 9) with silver triflate and isolated in ~ 73 - 80 % yield after purification. During the ion metathesis, as expected, silver bromide precipitated in methanol. The cyclic voltammogram (Figure 57) shows a general description of adsorption of resorcinarene quaternary ammonium cations on the surface of the Au electrode in the absence of bromide anions. We observed that there were no reversible adsorption/desorption peaks with all three resorcinarene triflate 10–12 surfactants. However, in the case of resorcinarene triflate 10 the reductive current in between -0.6 and -0.8 V was much stronger than that of the other resorcinarenes triflates 11 and 12 and the background. The intensity of the reductive current in the CV between -0.6 and -0.8 V is very similar to the order of stability of the gold nanoparticles prepared in the presence of resorcinarenes 7–9 being most stable has largest intensity while the dispersion being least stable has smallest intensity. Further, similar to the observations of Burgess and coworkers, we observed that the capacitive currents (-0.50 to -0.10) of all three resorcinarene triflates were narrower than those of the electrolyte (TBAP), suggesting the adsorption of resorcinarene cations on the electrode surface. A closer look revealed the capacitive currents of resorcinarene 12 were much narrower than those of the other resorcinarene surfactants, which could perhaps be attributed to the blocking by bulky headgroups.
Scheme 6. Ion metathesis of resorcinarene quaternary ammonium triflates.

7 = -Pyridine
8 = -NMe₃
9 = -NBu₃
-R' = -C₆H₁₃
3.6. Stability studies in the presence of cationic and anionic dyes

We further evaluated the stability of gold nanoparticles prepared in the presence of resorcinarene 7 by introducing cationic and anionic dyes. Parkin and coworkers have reported the interaction of citrate stabilized gold nanoparticles with a range of cationic and anionic dyes. They showed that the interaction between cationic dyes and negatively charged citrate stabilized gold
nanoparticles induced the formation of aggregates and enhancement of absorption corresponding to the aggregation peak.\textsuperscript{337,338} As the amount of cationic dye addition increases, the nanoparticles began to fragment and agglomerate into larger clusters up to several micrometers in size.\textsuperscript{337,338} However, anionic dyes did not lead to the formation of aggregation or any enhancement of dye absorption.\textsuperscript{337,338} Therefore, they suggested that the charge on the dyes plays a major role in the electrostatic attraction or repulsion between the dye molecules and the nanoparticle surface.\textsuperscript{337,338}

We titrated various dyes with a constant amount of gold nanoparticles prepared in the presence of resorcinarene 7 (Figure 58 – 60). The UV-vis titration spectra of cationic rhodamine 6G with gold nanoparticles showed no interaction between the dye molecules and gold nanoparticles (Figure 58). While the intensity of the nanoparticle peak decreased as the titration progressed, the intensity of the dye absorption increased. No additional peaks corresponding to the aggregation of the nanoparticles were observed.

![Figure 58. UV-vis titration spectra of gold nanoparticles prepared in the presence of resorcinarene surfactant 7 with aliquots of 20 \(\mu\)M rhodamine 6G stock solution.](image)
In the case of crystal violet, Parkin and coworkers reported the enhanced absorption of crystal violet at a critical concentration (1.52 µM) upon addition to a gold nanoparticle solution. Upon addition of cationic crystal violet, the extinction maxima in the UV-vis spectra progressively shifted from 525 nm corresponding to the LSPR of gold nanoparticles prepared in the presence of resorcinarene surfactant 7 to 573 nm corresponding to the absorption maxima of cationic crystal violet dye. No additional peaks corresponding to the aggregation of the nanoparticles were observed. Thus, the titration of crystal violet with the gold nanoparticles prepared in the presence of resorcinarene surfactant 7 showed no electronic interaction and no aggregation behavior (Figure 59).

![Figure 59. UV-vis titration spectra of gold nanoparticles prepared in the presence of resorcinarene surfactant 7 with aliquots of 20 µM crystal violet stock solution.](image-url)
We also tested the effect of brilliant blue G, an anionic dye (Figure 60). Due to limited solubility of brilliant blue G in chloroform, a stock solution of 0.2 mM was prepared and the insoluble materials were removed at this stage by filtration/decantation. Hence, we cannot precisely pinpoint the exact concentration of brilliant blue G employed in this study. We observed that the absorbance of gold nanoparticles decreased from 0.60 to 0.32 as the titration progressed. However, we did not see any interaction between this anionic dye and the cationically charged pyridinium functionalized nanoparticles and the nanoparticles were stable. Thus, gold nanoparticles prepared in the presence of resorcinarene 7 showed excellent dispersion stability in organic medium even in the presence of cationic or anionic dyes.

Figure 60. UV-vis titration spectra of gold nanoparticles prepared in the presence of resorcinarene surfactant 7 with aliquots of brilliant blue G stock solution.
Consistent with UV-vis studies, TEM analysis also showed that there were no shape or size change in the Au nanoparticles in the presence of cationic or anionic dyes (Figure 61). The size analyses revealed average dimensions of 7.4 ± 1.9 nm (n = 131), 7.3 ± 2.1 nm (n = 135), and 7.4 ± 1.8 nm (n = 133) in the presence of rhodamine 6G, crystal violet, and brilliant blue G, respectively. Note that these dimensions agreed well with the dimensions of the parent nanoparticles prepared in the presence of resorcinarene surfactant 7.

![Figure 61. TEM images of (a) Au nanoparticles prepared in the presence of resorcinarene surfactant 7 and the same in the presence of (b) rhodamine 6G, (c) crystal violet and (d) brilliant blue G.](image)
3. 7. Ligand mediated phase-transfer studies

We also investigated the extraction of gold nanoparticles prepared in the presence of resorcinarene surfactant 7 from the organic phase into the aqueous phase mediated by 4-dimethylaminopyridine (DMAP). As shown in Figure 62, we observed the transfer of gold nanoparticles mostly into the interface and some into the aqueous phase. Notably, the organic phase which was initially dark pink became colorless during this process. To enhance the dispersion of gold nanoparticles into the aqueous phase, another identical sample was heated at 50 °C for 90 min (Figure 62c). However, there was no visible improvement in the transfer of nanoparticles into the aqueous phase. This visual observation is consistent with the absorbance intensities of the nanoparticles in the aqueous phases as seen in Figure 63a. When compared to the parent nanoparticles dispersed in the organic phase, the UV-vis spectra revealed a significant red-shift (532 nm) and broadening of the LSPR peak of the gold nanoparticles in the aqueous phases (Figure 63b). The TEM analysis of the inverse extraction of gold nanoparticles prepared in the presence of resorcinarene 7 showed no noticeable changes in their average dimensions of 7.0 ± 1.7 nm (n = 166).
Figure 62. Photographs of (a) Au nanoparticles prepared in the presence of resorcinarene surfactant 7 in chloroform in the presence of water (as control), (b) Au nanoparticles prepared in the presence of resorcinarene surfactant 7 in chloroform in the presence of aqueous DMAP and (c) the gold nanoparticles partially extracted into aqueous phase by DMAP by heating at 50 °C for 90 min.
Figure 63. UV-vis spectra (a) of gold nanoparticles prepared in the presence of resorcinarene surfactant 7 in chloroform (blue), gold nanoparticles partially extracted into aqueous phase by DMAP (red), and gold nanoparticles partially extracted into aqueous phase by DMAP by heating at 50 °C for 90 min (green) and (b) their normalized UV-vis spectra.
3. 8. Synthesis of Au nanoparticles in the exclusive presence of resorcinarene surfactants

We wanted to employ these resorcinarene surfactants as both phase-transfer and stabilizing agents in the two-phase synthesis of nanoparticles and replace TOABr entirely. Brust-Schiffrin two phase synthesis is typically carried out mostly in toluene\textsuperscript{92} or chloroform\textsuperscript{341} medium. However, all these resorcinarenes were only partially dispersible in toluene. On the other hand, while resorcinarene 9 was completely soluble in chloroform, resorcinarene 8 could be partially dispersed and resorcinarene 7 was almost insoluble. We carried out two phase synthesis of gold nanoparticles in the exclusive presence of both resorcinarenes 8 in dichloromethane and 9 in chloroform. Understandably, while resorcinarene 9 could completely phase-transfer gold salts into chloroform, resorcinarene 8 could not completely phase-transfer gold salts into dichloromethane. During the synthesis of the nanoparticles we observed the formation of a significant amount of precipitate in the presence of resorcinarene 8, while the nanoparticles synthesized in the presence of resorcinarene 9 were visibly very stable without any noticeable precipitation. The TEM analysis of the nanoparticles formed in the exclusive presence of resorcinarene 9 showed an average dimension of 7.8 ± 2.9 nm (n = 221) (Figure 64a–b). TEM also showed the presence of some anisotropic triangular and elongated structures. The UV-vis analysis of these nanoparticles prepared in the presence of resorcinarene 9, showed the LSPR at 519 nm (Figure 64c). It is worth noting that the nanoparticles prepared in the presence of both resorcinarene 9 and TOABr also showed both anisotropic structures and had LSPR at 519 nm. The UV-vis analysis of the gold nanoparticles prepared in the exclusive presence of resorcinarene 8 in dichloromethane showed the LSPR at 528 nm (Figure 64d). Again, this matched well with the LSPR of the nanoparticles prepared in the presence of both resorcinarene 8 and TOABr. Though these preliminary studies show that resorcinarene surfactant 9 can indeed act as both a phase-transfer agent for metal salts and a stabilizer of gold nanoparticles, the successful implementation and large-scale application of these surfactants require increased solubility in relatively non-polar solvents including toluene which is widely employed in Brust-Schiffrin synthesis. The solubility of resorcinarene surfactants in non-polar solvents could perhaps be improved by increasing their hydrocarbon chain lengths.
4. Summary

We have developed a simple method for the extraction of citrate stabilized gold nanoparticles into organic solvents using multidentate ionic resorcinarenes 7–9. This approach allows the dispersion of relatively larger gold nanoparticles (up to 29 nm) in organic solvents, hitherto inaccessible by other ionic surfactants. The phase transfer process and the resulting nanoparticles have been characterized by TEM, EDS, UV-vis, and IR. The long-term dispersion stability of these nanoparticles in organic solvents depended on the nature of the ionic headgroup.
of the resorcinarene surfactants, and the dispersions stabilized by resorcinarene 7 were stable for several weeks under ambient conditions. Further the nanoparticles stabilized by resorcinarenes 7 and 8 were also stable against thiourea induced aggregation\textsuperscript{347} in both aqueous and organic medium. Resorcinarenes 7 and 8 also endowed the nanoparticles with excellent processability, and they could be precipitated and redispersed in organic solvents without any irreversible aggregation. Though we have demonstrated the ability of resorcinarenes to extract and stabilize gold nanoparticles, this approach can be readily applied to other citrate stabilized mono- and bimetallic nanoparticles\textsuperscript{346,358} with implications in a number of applications including catalysis.\textsuperscript{153}

We have shown the direct synthesis of gold nanoparticles in the presence of multidentate resorcinarene quaternary ammonium surfactant (7–9) under Brust-Schiffrin conditions. The presence of resorcinarene 7 and 8 led to the formation of relatively smaller sized nanoparticles which were also more stable. However, in the presence of resorcinarene 9 polydisperse nanoparticles including some anisotropic nanostructures were obtained. Consistent with the recent literature,\textsuperscript{351,352} our electrochemical investigations suggest that these quaternary ammonium resorcinarene surfactants can be adsorbed on the Au surfaces even in the absence of bromide counterions. The differential stabilization of nanoparticles by these surfactants could perhaps be attributed to the differential interaction of these resorcinarene surfactants with the bromide anion and or their direct interaction with the nanoparticle surfaces. Gold nanoparticles prepared in the presence of resorcinarene surfactant 7 revealed exceptional dispersion stability for several weeks. These nanoparticles also showed excellent robustness in the presence of cationic and anionic dyes. On the other hand, such gold nanoparticles prepared in the presence of resorcinarene 7 could be partially extracted into the aqueous phase from the organic phase. We have also shown the synthesis of gold nanoparticles in the exclusive presence of resorcinarene surfactants (8 and 9) without the aid of TOABr under the Brust-Schiffrin conditions.
CHAPTER 5

NANOCAPSULES AS TEMPLATE REACTION VESSELS FOR THE IN SITU SYNTHESIS AND AGGREGATION OF METAL NANOPARTICLES

1. Introduction

Nanosized capsules replicating the capsid structure of viruses, are currently being developed for wide-ranging applications from functional materials to drug delivery. Nanocapsules have attracted increasing interest in recent years due to their capability to encapsulate large quantities of guest molecules within their empty core domain. They have been utilized as drug carriers and nanoreactors with applications in synthesis and catalysis.

Synthetic approaches for the preparation of nanocapsules involve self-assembly, emulsion polymerization, and sacrificial templates including dendrimers. Self-assembled nanocapsules mimicking biological systems have been explored in detail. For instance, the aggregation of amphiphilic lipid molecules leads to hollow bilayer structures such as vesicles or liposomes. Amphiphilic block copolymers, typically consisting of both hydrophilic and hydrophobic blocks, can also aggregate into vesicular structures in aqueous solution. Depending on their hydrophilic fractions, the amphiphilic block copolymers can also self-assemble into rod-like aggregates, micelles or vesicles. The main drawback of such a method is the limited in vivo applicability.

Hollow polymer capsules can also be prepared via emulsion/suspension polymerization techniques. In an oil-in-water emulsion, the oil phase consists of a mixture of a polymer which forms the shell, a volatile solvent and a non-volatile solvent. A large amount of volatile solvent is required to dissolve the polymer in aqueous phase. As the volatile solvent evaporates, the polymer is precipitated and the droplets containing the polymer shrink in size. Continual evaporation of the volatile solvent will allow more polymer precipitates to migrate resulting in the formation of hollow polymeric capsules. Another convenient method involves the polymerization of a different monomer on a latex particle (as a core) obtained by
conventional emulsion polymerization and the subsequent removal of the core.\textsuperscript{359} This process is quite simple conceptually but the harsh conditions, such as continual base and acid treatment at high temperature, are required for removal of the latex cores.\textsuperscript{367}

Another approach to generate nanocapsules is to form an organic/polymeric shell around a preformed sacrificial template which will be subsequently removed to form nanocapsules.\textsuperscript{370} This is a powerful technique where size of the capsules can be tuned by appropriate template dimensions.\textsuperscript{370} A number of sacrificial templates including silica\textsuperscript{370} and gold nanoparticles,\textsuperscript{371} and self-assembled amphiphilic block copolymers\textsuperscript{366} have been exploited. A popular templating method is the layer-by-layer (LbL) assembly of polymers onto sacrificial polymeric or inorganic templates for the fabrication of polymeric multilayer capsules (PMLC).\textsuperscript{360} These LbL assemblies proceed via electrostatic assembly of oppositely charged polyelectrolytes, hydrogen bonding involving polymers, and additional covalent modifications.\textsuperscript{360,361} These nanocapsules showed initial potential for drug delivery purposes as \textit{in vitro} carrier systems, but the use of non-degradable polyelectrolytes results in limited \textit{in vivo} applicability.\textsuperscript{372}

Dendrimers or hyperbranched polymers have also been employed for the fabrication of nanocapsules.\textsuperscript{373,374} Dendrimers with homo-allyl ether groups on their periphery could be intramolecularly cross-linked via a ring-closing metathesis reaction and the subsequent removal of the core by hydrolysis leads to the formation of nanocapsules.\textsuperscript{375} However, this dendrimer approach is rather expensive and a tedious procedure is involved in the core removal process.\textsuperscript{367}

The thiol-ene reaction is the formal addition of thiol to a non-activated double bond. The "click" reactions have attracted enormous attention due to their potential and selectivity for the synthesis of new compounds through heteroatom links (C-X-C).\textsuperscript{376-378} The term "click chemistry" was introduced and described by Sharpless in 2001.\textsuperscript{376} There are several recognizable "click" characteristics, in the thiol-ene reaction that make it a facile and versatile process.\textsuperscript{376,379,380} For example, such reactions (a) can proceed under mild and solventless conditions, (b) include readily available and easily manipulable starting compounds as well as orthogonality with other organic synthesis reactions, (c) are insensitive to the presence of air/oxygen and moisture, and (d) proceed rapidly in a regioselective fashion and result in high yields with by-products (if any) that are easily removable. This thiol-ene reaction has been widely used in surface and particle
patterning, polymer and nanoparticle modification, synthesis of new homogeneous and hybrid network structures, stabilization of capsules and multilayer systems, and preparation of microfluidic devices.

Mechanistically the thiol–ene reaction actually proceeds via a radical step-growth pathway. UV radiation initiates cleavage of the sulfur-hydrogen bond to form a thiol radical (equation 9). Propagation revolves around the addition of the thiol radical across the vinyl functional group to yield an intermediate carbon centered radical (equation 10). This is followed by a transfer of the radical to a thiol functional group producing the thiol–ene product (equation 11). During this course a new thiol radical is concomitantly generated. Termination reactions occur by typical radical–radical coupling processes.

\[
RS\cdot \xrightarrow{h\nu} RS\cdot + H\quad (9)
\]

\[
RS\cdot \xrightarrow{R'} R'_1-S-R'\quad (10)
\]

\[
R'_1-S-R' + RS\cdot \xrightarrow{RS-H} R'_1-S-R' + RS\cdot \quad (11)
\]

Thiol–ene photopolymerization has been recently emerging as a new, direct, template-free technique for the synthesis of nanocapsules. Kim and coworkers reported that the photopolymerization of a cucurbituril-alkene monomer with dithiol linkers led to the direct formation of nanocapsules. These polymeric nanocapsules prepared in methanol have an average size of 100 ± 30 nm with an average shell thickness of 2.1 ± 0.3 nm. The atomic force microscopy (AFM) analysis of these nanocapsules showed an average height of 40 ± 6 nm, indicating some flattening of the nanocapsules. They have investigated the effects of various factors such as solvents, monomer concentrations, and temperatures on the formation of polymeric nanocapsules obtained by thiol–ene photopolymerization. They showed that polymerization in chloroform and acetonitrile yielded polydisperse nanocapsules with an average size of 600 ± 100 nm and 150 ± 50 nm, respectively. However, polymerization in N,N-dimethylformamide resulted in both nanocapsules and rolled or folded thin films. Notably the relationship between various solvents and the formation of nanocapsules is not clear. In
general in step-growth polymerization, the molar ratio of monomers can influence the formation of the nanocapsules due to the altered molecular weight of the resulting polymeric products. At higher concentrations of dithiol and or cucurbituril-alkene, the diameter of the nanocapsules gradually increased. Increasing the polymerization temperature also increased the dimensions of the nanocapsules.

Balasubramanian and coworkers showed that resorcinarene tetra alkene tetra thiol 12 (RTATT), a single-component multi-thiol and multi-alkene (ene) monomer, can also be photopolymerized into hollow polymeric nanocapsules. In addition to nanocapsules, they showed a variety of polymeric architectures can be obtained by photopolymerization by varying the polymerization media. While polymerization in chloroform led to the formation of nanocapsules with an average size of 106 ± 18 nm, in dichloromethane the photoproducts have a network lattice structure with nano and micrometer sized pores. Polymerization in ethyl acetate showed fibrous structures, and tetrahydrofuran showed spherical polydisperse nanoparticles with an average size of 85 ± 53 nm. They suggested that the formation of various morphologies could be due to two antagonistic effects: (1) the rate of the cross-linking reaction (or reaction extent) and (2) phase separation effect. IR analysis of the RTATT polymerization reaction showed higher reaction extent in both dichloromethane and ethyl acetate, in contrast to chloroform and tetrahydrofuran with lower reaction extent. The late onset of phase separation at higher reaction extent is known to produce web-like or sparse networks. Contrarily, the early phase separation at lower conversion results in the formation of spherical nanoparticles. They and others have also invoked the covalent lipid architecture model for the formation of hollow polymeric nanocapsules. Further, they also probed other factors including the monomer concentration and duration of polymerization, which can influence the morphological development. With lower RTATT concentrations in chloroform, photopolymerizations yielded both polydisperse nanocapsules and linear structures. Note that there were no significant changes in the size or shape of the nanocapsules for various polymerization durations (15 min and 20 h).
Polymer nanocapsules can potentially act as excellent 3-D substrates for nanoparticle assembly. The synthesis of polymeric nanocapsule–metal nanoparticle nanocomposites typically involves the embedding of the nanoparticles at a very early stage. Embedding nanoparticles directly into capsule like container molecules has been carried out but they typically result in low filling efficiency of nanoparticles. Hence, there exists a need to develop simple, tunable, modular approaches for the preparation of controlled hybrid architectures.

Our group recently showed that RTATT nanocapsules containing ubiquitous sulfide linkages and thiol functional groups can act as excellent 3D templates for the synthesis and assembly of noble metal nanoparticles and nanostructures. In principle, sulfur containing nanocapsules as templates could stabilize nanoparticles both inside and outside the polymer shell in distinct ways (Scheme 7). Our work demonstrated the synthesis of gold nanostructures using RTATT nanocapsules. We showed that the nature and shape of the gold nanostructure formed, i.e., the synthesis of gold nanoshells or spherical aggregates of gold nanoparticles, depends on the
reaction conditions. Controlled formation of such noble metal nanostructures with tunable optical properties is expected to play a crucial role in SERS\textsuperscript{397,400} and catalysis applications.\textsuperscript{396} We have indeed shown the utility of such RTATT nanocapsule templated gold nanoparticle aggregates in the reduction of 4-nitrophenol (equation 12).

\begin{equation}
\begin{array}{c}
\text{NO}_2 \\
\text{OH} \\
\end{array} + \text{NaBH}_4 \xrightarrow{\text{Catalyst}} \begin{array}{c}
\text{NH}_2 \\
\text{OH} \\
\end{array}
\end{equation}

This work will focus on two-component photopolymerization using resorcinarene monomers. The objective of this work is to undertake a systematic investigation of the influence of the valency of the alkenes in the two-component photopolymerization of resorcinarene benzylthiol building blocks. We hypothesized that by having the thiol and ene functional groups in different molecules (monomers) we may be able to better control the mechanical properties of the nanocapsules (polymer) by independently varying the monomers (Figure 65). Given the stoichiometry of the thiol-ene reaction, we will employ a 1:1 ratio of thiol:ene in these reactions. In contrast to this work, note that Kim and coworkers have used a thiol:ene ratio of 8:1 to generate cucurbituril nanocapsules.\textsuperscript{390,391} However, the authors did not provide specific reasons for the stoichiometry employed. Another major objective of this work is to use polymeric resorcinarene nanocapsules as template reaction vessels for synthesizing platinum nanocomposites and use them in catalytic applications.
2. Experimental section

2.1. General remarks

1, 9-Decadiene (Alfa Aesar, 97 %) and Triallyl-S-triazine-2,4,6(1H,3H,5H)-trione (Acros Organics, 98 %) were obtained from commercial sources and used as received, without further treatment. Bromochloro methane (Alfa Aesar, 98 %) and cesium carbonate (Alfa Aesar, 99 %) were used as received. Hydrogen hexachloroplatinate (Acros Organics, 99.9 %), tetraoctylammonium bromide (TOABr) (Alfa Aesar, 98+ %), and sodium borohydride (Sigma
Aldrich, 98+ %) were used as received without any further treatment. Synthesis of Resorcinarene tetra alkene tetra thiol 12 (RTATT) has been described elsewhere.401 All organic solvents were commercially available and distilled before use. Barnstead Nanopure water (18.2 MΩ • cm) was used for all syntheses. All glasswares used were silanized.

2. 2. Synthesis of resorcinarene benzylthiol 4

Please refer to Chapter 2. 2. 5. for the synthesis of resorcinarene benzylthiol and associated characterization.

2. 3. Synthesis of resorcinarene tetraene 16

To an ice cold solution of resorcinol (6.09 g, 0.055 mol) and 10-undecenal (11.2 mL, 0.056 mol) in ethanol (65 mL), conc. HCl (8 mL, 12.1 N) was added dropwise. The reaction mixture was refluxed at 65 °C for 14 h under argon atmosphere (Scheme 8). After cooling to room temperature, the reaction mixture was poured into cold water (150 mL). The precipitate obtained was filtered and washed with copious amounts of water until the pH of filtrate was neutral. After drying for a day under vacuum, the crude product was obtained and reprecipitated by addition of water to acetonitrile solution. The precipitate obtained was filtered and dried to yield the title compound as a solid (13.44 g, 93 %). $\nu_{\text{max}}$/cm$^{-1}$: 3255 (b) 2930 2855 1619 1502; $\delta_H$ (400 MHz,CDCl$_3$): 9.58 (m, 8H), 7.21 (s, 4H), 6.13 (s, 4H), 5.81 (m, 4H), 4.95 (m, 8H), 4.31 (s, 4H), 2.22 (s, 8H), 2.06 (q, $J = 8$ Hz, 8H), 1.39 – 1.26 (m, 48H).

2. 4. Synthesis of resorcinarene tetraene cavitand 17

Resorcinarene tetraene 16 was synthesized from resorcinol and 10-undecenal by a modified literature procedure.401,402 To a solution of resorcinarene tetraene 16 (2.2 g, 0.002 mol) in DMF (70 mL) in a heavy walled pressure vessel, Cs$_2$CO$_3$ (13.0 g, 0.399 mol) and CH$_2$BrCl (13.9 g, 0.108 mol) were added and stirred at 80 °C. After 12 h, the reaction mixture was allowed to cool to room temperature. The reaction mixture was poured into a 2N HCl solution (150 mL), and extracted with diethyl ether (250 mL). The extracted organic phase was washed with copious amounts of water and dried over MgSO$_4$. After removal of volatiles, the crude product obtained was purified by column chromatography to yield the title compound as a solid (0.726 g, 23 %). $\nu_{\text{max}}$/cm$^{-1}$: 3438 (b), 3075, 2926, 2853, 1640, 1491, 994; $\delta_H$ (400 MHz,CDCl$_3$): 7.11 (s, 4H), 6.49
(s, 4H), 5.87–5.77 (m, 4H), 5.76 (d, J = 7.2 Hz, 4H), 5.03–4.93 (m, 8H), 4.73 (t, J = 8 Hz, 4H), 4.45 (d, J = 7.2 Hz, 4H), 2.22 (q, J = 7.2 Hz, 8H), 2.06 (q, J = 7.2 Hz, 8H), 1.42–1.26 (m).

Scheme 8. Synthesis of resorcinarene tetraene cavitand 17.

2.5. Two-component thiol-ene photopolymerization

To a solution of resorcinarene benzylthiol 4 (8.1 mg, 1.5 mM) in chloroform (5 mL), alkene monomer 14 (3 mM of 1, 9-decadiene) or 15 (2 mM of triallyl-S-triazine-2,4,6(1H,3H,5H)-trione) or 17 (1.5 mM of resorcinarene tetraene cavitand) was added. This resulting solution was filtered through a 0.45 µm nylon membrane and transferred into a quartz tube. The mixture was degassed with argon for 2 min and sealed, prior to UV irradiation for 3 h. Photopolymerization was carried out at room temperature in a Srinivasan–Griffin photochemical reactor equipped with four 254 nm and four 300 nm lamps. Aliquots of the photoproducts were transferred into a spectra pour membrane (6000 – 8000 molecular weight cut off) and dialyzed in a mixture of
chloroform and methanol (3:1). After removal of volatiles from the dialyzed samples, the yields of these photoproducts obtained were calculated by mass recovery.

2.6. Synthesis of RTATT nanocapsules

A solution of RTATT 13 (20.5 mg, 0.017 mmol) in chloroform (11 mL) was filtered through a 0.45 µm nylon membrane and transferred into a quartz tube and degassed with argon for 30 s and sealed, prior to UV irradiation for 3 h as described earlier.

2.7. Synthesis of platinum nanoaggregates using RTATT nanocapsules

An aqueous solution (3 mL) of H₂PtCl₆ (16 mg, 0.031 mmol) was vigorously stirred for 30 min with a solution of TOABr (49.2 mg, 0.090 mmol) in chloroform (5 mL) at room temperature under argon atmosphere. During stirring, the color of the aqueous phase changed from yellow to colorless, while that of the organic phase changed from colorless to yellow. After discarding the aqueous phase, the organic phase containing the metal salt was transferred into a new reaction vessel and RTATT nanocapsules (7.45 mg, 0.006 mmol) in chloroform (4 mL) were added and stirred for 30 min. The reaction mixture was then cooled to 0 °C and a freshly prepared solution of sodium borohydride (15.2 mg, 0.402 mmol) in ice cold water (1 mL) was added and vigorously stirred at 0 °C for 1 h. The color of the reaction mixture transitioned from yellow to brown in a minute after the addition of sodium borohydride. The organic phase was collected and washed with copious amounts of nanopure water (10 mL × 3).

2.8. Characterization

Transmission electron microscopy (TEM) was used to confirm the size and morphology of photopolymers and nanocomposites. The TEM samples were prepared on a carbon-coated grid. Due to intrinsic lack of contrast of organic polymers, staining agents (uranyl acetate or osmium tetroxide) were employed. Osmium tetroxide adheres to the polymer by reacting with double bonds which was used to measure the thickness of the nanocapsule shell. Atomic forces microscopy (AFM) was performed to determine the height, size, and morphology of nanocapsules. FT-IR was used to monitor the thiol-ene polymerization progression.
3. Results and discussion

3.1. Direct synthesis of polymeric resorcinarene nanocapsules with tunable shell thickness and rigidity

In this work, resorcinarene benzylthiols were reacted with alkenes of various valencies (Figure 65). A solution of resorcinarene benzylthiol 4 (a) and alkenes 14, 15 and 17 (b–d) in chloroform were irradiated with 254 nm and 300 nm lamps for 3 h. Given the success of our group’s earlier results, these photopolymerization reactions were carried out in chloroform. Note that the benzylic thiol group present in resorcinarene cavitand 4 is more reactive than the thiophenol based monomers employed in our earlier studies. Among the ene monomers, diene 14 and tetraene 17 are slightly more reactive than triene 15 in the thiol-ene photopolymerization. After 3 h of UV irradiation, the FT-IR spectra (Figure 66) of the resulting products show that the thiol (-SH) stretch at 2563 cm\(^{-1}\) disappeared completely in all three photoproducts, though some residual alkene peak at 1650 cm\(^{-1}\) (C=C) still remained. The oligomeric species and unreacted monomers were eliminated by dialysis. Subsequent to the dialysis we estimated the yields of the resulting pure photoproducts. The yields of these photopolymerization reactions varied somewhat depending on the monomer. For example, while the reaction of resorcinarene benzylthiol 4 with triene monomer 15 gave a yield of 79%, the polymer formed with diene 14 was obtained in 51% yield.
Figure 66. FT-IR spectra of resorcinarene benzylthiol 4 monomer (a) and its photoproducts with diene 14 (b), triene 15 (c), and tetraene 17 (d). These reactions were subjected to UV irradiation for 3 h.
Figure 67. TEM images of photoproducts obtained from resorcinarene benzylthiol 4 with diene 14 (a–b), triene 15 (c–d), and tetraene 17 (e–f). These images were obtained after staining the samples with either OsO$_4$ or uranyl acetate. The yellow lines indicate the shell thickness of the nanocapsules.

The morphology of various photoproducets was probed by TEM (Figure 67). Due to inherent low contrast, the photopolymers were stained with OsO$_4$ or uranyl acetate for TEM analysis. In all three cases, spherical objects with a darker rim and lighter core were observed, indicating the formation of hollow nanocapsules. Contrary to the work of Kim and coworkers,$^{391}$ these nanocapsules are prepared from a rigid multi-thiol resorcinarene monomer and flexible alkene
building blocks. Kim and coworkers have prepared hollow nanocapsules using a rigid multi-
alkene cucurbituril monomer and flexible di-thiol linkers. These studies suggest that one of the
building blocks, either thiol or ene should be present in a somewhat rigid environment for the
formation of nanocapsules using thiol-ene photopolymerization. The nanocapsules formed from
diene 14, triene 15, and tetraene 17 showed average dimensions of 130 ± 40 nm (n = 21), 100 ±
50 nm (n = 215), and 120 ± 50 nm (n = 28), respectively.

Figure 68. TEM image (scale bar = 500 nm) of the nanocapsules from resorcinarene benzylthiol
4 and diene 14. This sample was stained with OsO₄.
Remarkably TEM analysis showed that the wall thickness of the nanocapsules obtained varied significantly in all three cases. In fact with OsO\textsubscript{4} staining at lower magnifications (Figure 68), hollow nanocapsules with thicker shells appeared like dark solid spheres. While the nanocapsules obtained from diene 14 had the thickest shell (24 – 34 nm), the nanocapsules obtained from tetraene 17 had the thinnest shell (~ 3 nm). Interestingly, the thickness of the nanocapsules shell obtained from triene 15 was ~ 18 – 29 nm. Note that there are some differences in the shell thickness between nanocapsules obtained in the same batch (Figure 69).

Figure 69. TEM images of the nanocapsules obtained from resorcinarene benzylthiol 4 and diene 14 (a), triene 15 (b).
Figure 70. AFM analysis of nanocapsules from resorcinarene benzylthiol 14 with diene 15 (a), triene 15 (b), and tetraene 17 (c).

These dimensions obtained from TEM were further confirmed by AFM analysis (Figure 70). The histograms of the size distribution are summarized in Figure 71. Unlike nanocapsules obtained in the presence of diene 14, nanocapsules obtained from triene 15 showed a bimodal size distribution centered around 75 and 125 nm with ~72% of the former. Similarly nanocapsules obtained from tetraene 17 also showed a bimodal size distribution centered around 65 nm (~68%) and 105 nm (~32%).
Figure 71. Histogram of dimensions measured from AFM analysis of nanocapsules from resorcinarene benzylthiol 4 with diene 14 (a), triene 15 (b), and tetraene 17 (c).

Table 3. Summary of the average dimensions of resorcinarene nanocapsules obtained by AFM and TEM analysis.

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<th>TEM</th>
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<tr>
<td></td>
<td>Height (nm)</td>
<td>Diameter (nm)</td>
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<tr>
<td>Diene (3h)</td>
<td>60 ± 10</td>
<td>150 ± 30</td>
</tr>
<tr>
<td>Triene (3h)</td>
<td>30 ± 10</td>
<td>90 ± 30</td>
</tr>
<tr>
<td>Tetraene (3h)</td>
<td>30 ± 10</td>
<td>80 ± 20</td>
</tr>
<tr>
<td>Triene (15min)</td>
<td>20 ± 10</td>
<td>90 ± 30</td>
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Unlike larger capsules which completely collapse upon drying, these nanocapsules did not fully flatten upon drying. The average height of these nanocapsules is summarized in Table 3. The nanocapsules obtained from diene 14 have a height of 60 ± 10 nm, higher than those obtained from triene 15 (30 ± 10 nm) and tetraene 17 (30 ± 10 nm).

It is worth noting that the height:diameter ratio of nanocapsules measured from AFM analysis systematically changed with the valency of the alkene monomers (Table 3). The height/diameter ratio indicates the rigidity or flexibility of the nanocapsules. Note that a higher ratio is expected for more rigid nanocapsules and a lower ratio is expected for more flexible nanocapsules. Such mechanical factors are crucial in determining the internalization, distribution, and circulation of nanocapsules. These results also showed the rigidity of the photoproduct increases as the valency of the alkene monomers decreases from tetraene 17 to triene 15 to diene 14. These results parallel the thickness of these nanocapsules; i.e., the thicker nanocapsules were also more rigid than the thinner ones. It is worth noting that Zimmerman and coworkers have shown that the rigidity of dendrimers can be altered by varying the extent of crosslinking. Highly cross-linked dendrimers showed an increased height in AFM analysis in air. It is possible that these thicker shells could also be highly cross-linked leading to the formation of more rigid nanocapsules. However, a thicker shell alone cannot explain a rigid nanocapsule. For example, in spite of distinct differences in shell thickness between nanocapsules obtained from triene 15 and tetraene 17, these nanocapsules revealed only a minor difference in the height/diameter ratio. We also probed the effect of photopolymerization duration in the formation of the nanocapsules. With shorter photopolymerization durations (15 min), as expected the rigidity of the nanocapsules significantly decreased, due to a smaller amount of crosslinking.

Though the mechanism of nanocapsule formation with varying thickness under two-component thiol-ene photopolymerization is unclear, we believe that the orientation and valency of the alkene building blocks may play a significant role in the morphological development of these photoproducts. It is possible that the formation of nanocapsules with varying thickness could be due to the formation of 2D oligomeric patches with varying thickness at the early stage of the photopolymerization.
3. 2. Synthesis of platinum nanocomposites with nanocapsules as template reaction vessels

To test the feasibility of using nanocapsules as reaction vessels, well-studied RTATT nanocapsules were chosen as model compounds. Recently, we demonstrated that the RTATT nanocapsules could operate as multivalent templates for the synthesis and self-assembly of gold nanostructures.\textsuperscript{236} This approach exploits the number of sulfide and unreacted thiol functional groups in these nanocapsules. Theoretically, nanocapsules have the ability to stabilize nanoparticles both inside and outside the polymer shell. Our work showed that the polymeric nanocapsule templates could form both metallic nanoshell and nanoaggregates depending on the reaction conditions.

Figure 72. TEM analysis of resorcinarene nanocapsule templated Pt nanoaggregates (a–d) and HRTEM image showing Moiré patterns (c–d).
For the synthesis and *in situ* aggregation of platinum nanoparticles using RTATT nanocapsules as template reaction vessels, the Brust-Schiffrin two-phase procedure was employed. Briefly, in the presence of RTATT nanocapsules, tetraoctylammonium stabilized Pt salts in chloroform were reduced with aqueous sodium borohydride at 0 °C for 1 h. TEM analysis of the product revealed the formation of both smaller individual Pt nanoparticles and much larger aggregated structures (Figure 72). These nanoaggregates show closely packed individual Pt spherical nanoparticles (typically 13.9 ± 3.2 nm), albeit larger than those of gold nanoparticle aggregates. The HRTEM image (Figure 72d) showed the presence of Moiré fringes which usually occur in TEM images from two superimposed crystal lattices. Very recently Kim and coworkers showed that cucurbituril based nanocapsules can also act as nanoreactors for the synthesis of Pd nanoparticles and their application in catalysis. In contrast to our work, the Pd nanoparticles prepared using cucurbituril nanocapsules were much smaller in dimensions (1.7 to 3.1 nm).

Table 4. Summary of the yield of propanol from the hydrogenation of allyl alcohol with the RTATT nanocapsule templated Pt nanoaggregates.

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<th>Yield (%) for time (h)</th>
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<td>RTATT nanocapsule templated Pt nanoaggregates</td>
<td>&lt;0.1 mg</td>
<td>42 % for 17 h</td>
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<td>100 % for 41 h</td>
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We tested the nanocapsule templated Pt nanoaggregates as catalysts in the hydrogenation of allyl alcohol to propanol (Table 4). To evaluate the catalytic activity of Pt nanoaggregates, the individual smaller nanoparticles were separated from the Pt nanoaggregates by a precipitation-redispersion cycle. The aggregates were precipitated by the addition of isopropyl alcohol to dispersions in chloroform in a volume ratio of 1:2 and centrifuged at 9 k rpm for 30 min. The precipitate (<1.0 mg) collected was redispersed in CDCl₃ for catalysis. The hydrogenation of allyl alcohol in the presence of Pt nanoaggregates yielded 42 % of propanol after 17 h; and 100 % after 41 h (Table 4). This observation is impressive as in general thiols with their strong passivating ability are known to poison or substantially reduce the catalytic activity of metal nanoparticles. For example, in the presence of the Pt nanoparticles prepared in the presence of resorcinarene benzylthiol (in Chapter 2) as catalysts only 2.6 % of propanol was obtained after 24 h in hydrogenation reaction of allyl alcohol. Hence weaker surfactants are often employed in the passivation of catalytic nanoparticles. On the other hand, macrocyclic surfactants such as cyclodextrin thiols have enabled the nanoparticles to remain catalytically active. Our observations are remarkable as we carried out this hydrogenation with 10-fold less loading of Pt nanocatalysts when compared with Kaifer's Pt nanocatalyst formed in the presence of cyclodextrin thiols¹¹⁴ which yielded >95 % in 6 hours.

4. Summary

This work shows that resorcinarene cavitand thiol can form hollow polymeric nanocapsules with a variety of alkenes. We have shown that the thickness of nanocapsules can be systematically changed by altering the valencies of the alkene building blocks. We also have demonstrated through TEM and AFM analysis that the rigidity of the nanocapsules increases as the shell thickness increases. The rigidity of nanocapsules can also be tuned by varying the duration of photopolymerization. This work also showed the utility of resorcinarene nanocapsules as template reaction vessels for the in situ synthesis and self-assembly of catalytic nanoparticles. Pt nanoaggregates templated in resorcinarene nanocapsules were prepared by a Brust-Schiffrin⁴³ type two-phase synthesis. Remarkably, these sulfide/thiol stabilized nanoparticles were active as hydrogenation catalysts and resulted in 100 % conversion even with low catalyst loadings.
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SELECTED PRESENTATIONS (Presenter name is underlined):
1. "Ionic resorcinarene surfactant stabilized gold nanoparticles", R. Balasubramanian, S. Han, presented in the 66th Southeastern Regional Meeting of the American Chemical Society, Nashville, TN, on October 18, 2014.

PATENT APPLICATION: