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Calix[n]arene-based Monolayer Protected Clusters (MPCs): Synthesis, Studies and Applications

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CHAPTER 1 - General introduction

Various materials were used by different cultures during history and for the anthropologists they represent a good way to define the civilization. The employment of more sophisticated and specific materials had as most important outcome an improvement of the people cultural level and helped the creation of important operas. All these results were obviously limited by the type and availability of the materials in use in that particular culture. As an example, in the "stone age" the rate of civilization was limited by the type of stone that could be found in the area where a culture was settling.

In the last century, the evolution of the modern sciences has allowed development of new materials such as the synthetic polymers. Moreover, the chemistry of silicon has been widely explored in order to devise new technological devices. This new phase of the technological development has prompted the birth of a new interdisciplinary discipline, involving several areas of science and engineering, currently known as the "modern materials sciences". This discipline investigates the relationship between the structure of materials and their properties. It includes elements of applied physics and chemistry, as well as chemical, mechanical, civil and electrical engineering.[1]

The macroscopic properties of the matter have been becoming less important since, in the last three decades, the attention of the scientists has been shifted to the micro and nano aspects of the materials. In this

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1. D. R. Askeland, P. P. Pradeep, *The Science & Engineering of Materials*, 5th edition, Thomson-Engineering, **2005**, ISBN 0-534-55396-6.

context, in 1959 Richard Feynman gave a talk titled "There's Plenty of Room at the Bottom".[2] Feynman described a process by which the ability to manipulate individual atoms and molecules might be developed, using one set of precise tools to build and operate another proportionally smaller set, so on down to the needed scale. In the course of this, he noted, scaling issues would arise from the changing magnitude of various physical phenomena: gravity would become less important, surface tension and Van der Waals attraction would become more important, etc. This talk was considered as the birth of both Nanosciences and Nanotechnology.[3]

A unique aspect of nanotechnology is the vastly increased ratio of surface area to volume present in many nanoscale materials which opens new possibilities in surface-based science. These include statistical mechanical effects as well as quantum mechanical effects. In the latter case a great importance has assumed by the "quantum size effect" where the electronic properties of solids are modified as the particle size is reduced. It is important to note that this effect does not come into play by going from macro to micro dimensions. However, it becomes dominant when the nanometer size range is reached. Additionally, a number of other physical properties changes when compared to macroscopic systems. The discover of this "new world" is the beginning of the Nano Age. Beyond the toxicity risks to human health and the environment which are associated with the first-generation of nanomaterials,

2. For an account of the talk and how people reacted to it, see: E. Regis, *Nano!*, Bantam Books Ltd, **1995**. ISBN: 0593027868

3. C. P. Poole Jr, F. J. Owens, *Introduction to Nanotechnology*, John Wiley & Sons, Hoboken New Jersey, **2003**. ISBN: 0-471-07935-9.

nanotechnology has a broader societal implications and poses broader social challenges. Social scientists have suggested that nanotechnology's social issues should be understood and assessed not simply as "downstream" risks or impacts. Rather, the challenges should be factored into "upstream" research and decision making in order to ensure technology development that meets social objectives.[4] It is reasonable to suggest that nanotechnology will build incrementally, as did the 18-19th century industrial revolution, until it gathers pace to drive a nanotechnological revolution that will radically reshape our economies and our way of life.

The field in which nanotechnology could in a short period help our society are various and goes from cheap and powerful energy generation to the improvement of drugs, diagnostics and organ replacement. Obviously, nanotechnology opens door to fantasy and let human mind fly about future applications in the field of nanomedicine and nanorobotics.

Figure 1.1. An imaginary nanorobots working on a red corpuscle.

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4. M. Kearnes, R. Grove-White, P. Macnaghten, J. Wilsdon, B. Wynne, *Science as Culture*, **2006**, *15*, 291-307.

CHAPTER 2

2.1 Nanoscience and nanotechnology

The word "nano" is referred to $1/1'000'000'000 (= 10^{-9})$. In term of length units 1 nm is 10^{-9} m and it represents the molecular length scale of small molecules such as n-hexane. Some confusion is often found when defining nanoscience and nanotechnology. It is erroneously believed that these two terms are synonymous, in fact they express two different approaches to the same problem. Nanoscience is a basic research field facing the problem "to understand matter at the nanoscale level". On the other hand, nanotechnology is a more applied field that concerns "manipulation and control of the matter at the nanoscale level". These research fields are mutually interconnected, thus requiring the collaboration between researchers having different scientific background.

The advent of nanotechnology was depicted in an exciting and visionary way by Eric Drexler in the mid '80s.[1] Later, he presented his ideas on nanosystems and molecular manufacturing in a more scientific (but essentially theoretical) way claiming the possibility of constructing a general purpose nanodevice, nicknamed the assembler.[2,3] Such a nanorobot should be able to build almost anything, including copies of

1. K. E. Drexler, *Engines of Creation. The Coming Era of Nanotechnology*, Anchor Press, New York, **1987**. ISBN: 0-385-19973-2
2. K. E. Drexler, *Nanosystems. Molecular Machinery, Manufacturing, and Computation*, Wiley, New York, **1992**.
3. E. Regis, *Nano!*, Bantam Books Ltd, **1995**. ISBN: 0593027868

itself, by atomic-scale precision, "pick-and-place" machine-phase chemistry (mechanosynthesis).[4]

The fascinating but, admittedly, somewhat abstract ideas of Drexler about the construction, futuristic use, and also frightening potential of nanomachines have been sceptically received by a large part of the scientific community.[5] In fact, the ideas of maneuvering atoms or making molecular mechanosynthesis, that seem so appealing to physicists, did not convince chemists who are well aware of the complexity and subtlety of bond-breaking and bond-making processes.[3]

2.2 The role of supramolecular chemistry in the nanosciences and nanomaterials

The miniaturization of components for the construction of useful devices and machines is currently pursued by the "top-down approach". This approach, which leads physicists and engineers to manipulate progressively smaller pieces of matter by photolithography and related techniques, has operated in an outstanding way up until this time. It is becoming increasingly apparent, however, that the top-down approach is subject to drastic limitations for dimensions smaller than 100 nm.[6] This

4. a) K. E. Drexler, *Sci. Am.* **2001**, *285*, 66; b) K. E. Drexler, *Chem. Eng. News* **2003**, *81*, 37.

5. a) D. E. H. Jones, *Nature* **1995**, *374*, 835; b) G. Stix, *Sci. Am.* **1996**, *274*, 94; c) G. Stix, *Sci. Am.* **2001**, 285, 26; d) G. M. Whitesides, *Sci. Am.* **2001**, *285*, 70; d) G. M. Whitesides, *Small*, **2005**, *1*, 172.

6. R. F. Service, *Science* **2001**, *293*, 785. For an interesting assessment of the state-of-the-art and future requirements of semiconductor technology, see: The International

size is very small by the standards of everyday experience (about one thousandth of the width of a human hair), but it is very large on the scale of atoms and molecules. Therefore, as stated R. P. Feynman in 1959, "*there is plenty of room at the bottom*"[7] for further miniaturization, but the top-down approach does not seem capable of exploiting such an opportunity. An alternative and most promising strategy to exploit science and technology at the nanometer scale is offered by the "bottom-up approach", which starts from nano- or subnanoscale objects (namely, atoms or molecules, see infra) to build up nanostructures. On these basis *Nanomaterials* are materials having a characteristic length scale less than about a hundred nanometres. The bottom-up approach is largely the realm of nanoscience and nanotechnology.[8] This is the reason why chemists, being able to manipulate atoms and molecules, are in an ideal position to contribute to the development of nanoscience and nanotechnology.

In the bottom-up approach to miniaturization one can distinguish two different limiting cases:

Case 1: Nanoscale "objects" characterized by a very simple chemical form (atoms, clusters of atoms, small molecules) not exhibiting any specific intrinsic function. Nevertheless, functions arise from ensembles of such objects. An examples of this kind of construction is when atoms or very simple molecules can be used to write a word of nanoscale

Technology Roadmap for Semiconductors (ITRS) 2003, available at http://public.itrs.net
7. R. P. Feynman, address to the annual meeting of the American Physical Society, 1959 (see http://www.zyvex.com/nanotech/feynman.html); For an account of the talk and how people reacted to it see chapter 4 in Ref. 3.
8. V. Balzani, *Small* **2005**, *1*, 278.

dimension on a surface. Figure 2.1 shows how the new millennium was celebrated by writing the figure "2000" on a Cu(211) surface using 47 individually placed CO molecules.[9]
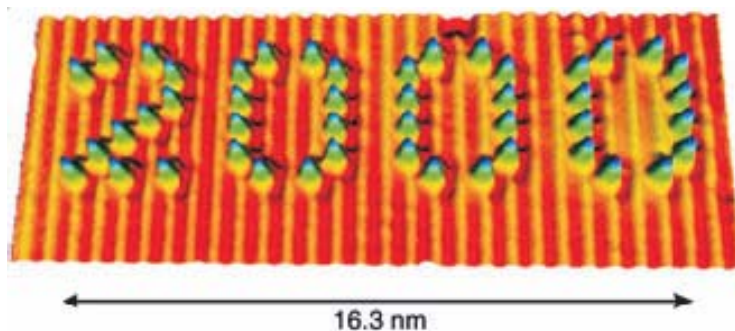

16.3 nm

Figure 2.1. The number 2000, celebrating the new millennium, has been written by using 47 CO single molecules. Each protrusion represents an individual CO molecule and the background vertical lines are the intrinsic Cu surface step edges.

Case 2: Nanoscale "objects" have complex chemical composition such as the multicomponent systems. These objects show peculiar properties and perform specific functions. The so called "artificial molecular devices and machines" belong to this category.[10] An example of such nanoscale "objects" is the prototype of a molecular muscle[11] (see Figure 2.2).

In the late '70s the research on molecular electronic devices began to flourish[12] and the idea arose[13] that molecules are much more convenient building blocks than atoms to construct nanoscale devices and machines.

9. S.-W. Hla, G. Meyer, K.-H. Rieder, *ChemPhysChem* **2001**, *2*, 361.

10. See *e. g.*: V. Balzani, L. Moggi, F. Scandola in *Supramolecular Photochemistry*, Ed.: V. Balzani, Reidel, Dordrecht, **1987**, p. 1.

11. M. C. Jiménez, C. O. Dietrich-Buchecker, J.-P. Sauvage, *Angew. Chem. Int. Ed.* **2000**, *39*, 3248.

12. a) A. Aviram, M. A. Ratner, *Chem. Phys. Lett.* **1974**, *29*, 277; b) F. L. Carter, R. E. Siatkowski, H. Wohltjen, *Molecular Electronic Devices*, Elsevier, Amsterdam, **1988**.

13. C. Joachim, J. P. Launay, *Nouv. J. Chim.* **1984**, *8*, 723.

The main reasons that provide the basis of this idea are as follows: (i) molecules are stable species, whereas atoms are difficult to handle; (ii) nature starts from molecules, not from atoms, to construct the great number and variety of nanodevices and nanomachines that sustain life; (iii) most laboratory chemical processes deal with molecules rather than with atoms; (iv) molecules are objects that already exhibit distinct shapes and exhibit device-related properties (e.g., properties that can be manipulated by photochemical and electrochemical inputs); (v) molecules can be covalently connected or (vi) can self-assemble to make larger structures. In the last context, a new branch of chemistry called *supramolecular chemistry* emerged and expanded very rapidly.[14] In particular, the formation of supermolecules results from the recognition directed spontaneous association of a well defined and limited number of molecular components under the intermolecular control of the non covalent interactions that held them together.

In the following years it became clear that Supramolecular chemistry, through the application of the "bottom-up approach" opens virtually unlimited possibilities[15] regarding the design of nanomaterials

14. Supramolecular Chemistry is defined as "the chemistry beyond the molecule, bearing on the organized entities of higher complexity, that result from the association of two or more chemical species held together by intermolecular forces", see : a) J.-M. Lehn, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 89; b) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**.
15. In the Foresight Update 20, Foresight Institute, Palo Alto, CA, it is reported that Roald Hoffmann reacted in this way when asked about the goal of nanotechnology: "I'm glad you guys (that includes women, of course) found a new name for chemistry. Now you have the incentive to learn what you didn't want to learn in college. Chemists have been practicing nanotechnology, structure and reactivity and properties, for two centuries, and for 50 years by design. What is exciting about modern

and nanoscale objects. As an example, it allows the construction of artificial molecular devices and machines capable of performing specific functions upon stimulation with external energy inputs[16] (see Figures 2.2). The "bottom-up approach" can also provide invaluable contributions to give a better understanding of the molecular-level aspects of the extremely complicated devices and machines that are responsible for biological processes.[17]

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nanotechnology is a) the marriage of chemical synthetic talent with a direction provided by "device-driven" ingenuity coming from engineering, and b) a certain kind of courage provided by those incentives, to make arrays of atoms and molecules that ordinary, no, extraordinary chemists just wouldn't have thought of trying. Now they're pushed to do so. And of course they will. They can do anything. Nanotechnology is the way of ingeniously controlling the building of small and large structures, with intricate properties; it is the way of the future, a way of precise, controlled building, with, incidentally, environmental benignness built in by design". www.foresight.org/Updates/Update20/Update20.1. html#anchor176004.

16. V. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines. A Journey into the Nanoworld*, VCH-Wiley, Weinheim, **2003**.

17. See *e. g.*: a) D. S. Goodsell, *Bionanotechnology: Lessons from Nature*, Wiley, New York, **2004**; b) M. Schliwa, *Molecular Motors*, Wiley-VCH, Weinheim, **2003**.
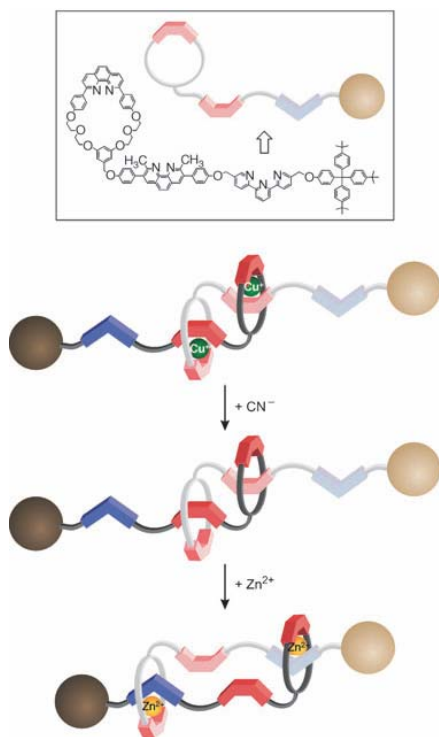
Figure 2.2 A prototype of a molecular muscle that respond to external stimuli.

2.3 Hybrid materials

The term *hybrid materials*[18] is used for many different systems spanning a wide area of different materials, such as crystalline highly ordered coordination polymers, amorphous sol–gel compounds, materials with and without interactions between the inorganic and organic units. The most wide-ranging definition is the following: a hybrid material is a material that includes two moieties blended on the molecular scale. Commonly one of these compounds is inorganic and the other one

18. *Hybrid Materials. Synthesis, Characterization, and Applications.* Ed: G. Kickelbick, Wiley-VCH, Weinheim, **2007**.

organic in nature. Judenstein proposed a classification based on the bonding chemical nature connecting the inorganic and organic pahses:[19]

Class I hybrid materials are those that show weak interactions between the two phases, such as van der Waals, hydrogen bonding or weak electrostatic interactions. In this class are included hybrids systems where one of the component (organic, biologic or inorganic), which can be molecules, oligomers or polymers is entrapped within a network of the other component.

Class II hybrid materials are those that show strong chemical interactions between the components. Because of the gradual change in the strength of chemical interactions it becomes clear that there is a steady transition between weak and strong interactions (Figure 2.3).

The frontier between both class is not always simple and we can eventually have hybrids systems with class I and class II characteristics. A typical example of such case are hybrids materials for optical applications made by encapsulation of organic chromophores within an hybrid matrix which belongs to class II. Although the dye interacts with the hybrid host via Van der Waals or Hydrogen bonding forces, the strong chemical bonds between organic and inorganic parts which make the host material has a significant impact on the overall properties of the system and therefore this kind of hybrids will be also classified as class II.

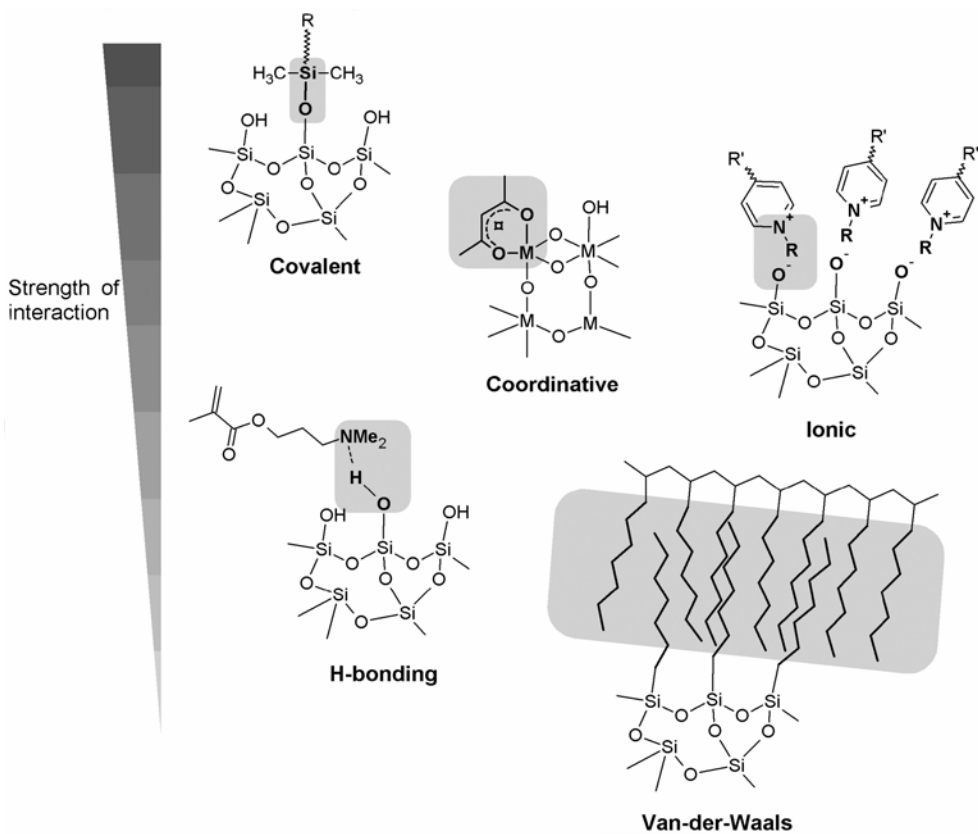19. P. Judenstien, C. Sanchez, *J. Mater. Chem.* **1996**, *6*, 511.

Figure 2.3. Selected interactions typically applied in hybrid materials and their relative strength.

The most obvious advantage of inorganic–organic hybrids is that they can favorably combine the often dissimilar properties of organic and inorganic components in one material. Because of the many possible combinations of components this field is very creative, since it provides the opportunity to invent an almost unlimited set of new materials with a large spectrum of known and as yet unknown properties. Another driving force in the area of hybrid materials is the possibility to create multifunctional materials. Examples are the incorporation of inorganic clusters or nanoparticles with specific optical, electronic or magnetic properties in organic polymer matrices. These possibilities clearly reveal

the power of hybrid materials to generate complex systems from simpler building blocks in a kind of LEGO © approach.

Probably the most intriguing property of hybrid materials that makes this material class interesting for many applications is their processing. Contrary to pure solid state inorganic materials that often require a high temperature treatment for their processing, hybrid materials show a more polymer-like handling, either because of their large organic content or because of the formation of crosslinked inorganic networks from small molecular precursors just like in polymerization reactions. Hence, these materials can be shaped in any form in bulk and in films. Although from an economical point of view bulk hybrid materials can currently only compete in very special areas with classical inorganic or organic materials, e.g. in the biomaterials sector, the possibility of their processing as thin films can lead to property improvements of cheaper materials by a simple surface treatment, e.g. scratch resistant coatings. Based on the molecular or nanoscale dimensions of the building blocks, light scattering in homogeneous hybrid material can be avoided and therefore the optical transparency of the resulting hybrid materials and nanocomposites is, dependent on the composition used, relatively high. This makes these materials ideal candidates for many optical applications. Furthermore, the materials' building blocks can also deliver an internal structure to the material which can be regularly ordered. While in most cases phase separation is avoided, phase separation of organic and inorganic components is used for the formation of porous materials.

Material properties of hybrid materials are usually changed by modifications of the composition on the molecular scale. If, for example, more hydrophobicity of a material is desired, the amount of hydrophobic molecular components is increased. In sol–gel materials this is usually achieved if alkyl- or aryl-substituted trialkoxysilanes are introduced in the formulation. Hydrophobic and lipophobic materials are composed if partially or fully fluorinated molecules are included. Mechanical properties, such as toughness or scratch resistance, are tailored if hard inorganic nanoparticles are included into the polymer matrix. Because the compositional variations are carried out on the molecular scale a gradual fine tuning of the material properties is possible.

One important subject in materials chemistry is the formation of smart materials, such as materials that react to environmental changes or switchable systems, because they open routes to novel technologies, for example electroactive materials, electrochromic materials, sensors and membranes, biohybrid materials, etc. The desired function can be delivered from the organic or inorganic or from both components. One of the advantages of hybrid materials in this context is that functional organic molecules as well as biomolecules often show better stability and performance if introduced in an inorganic matrix.

In the hybrid materials classifications can be also included the Self-assembled monolayers on surfaces (SAMs).[20] The term self-assembled monolayers (SAMs) is used to described organized molecular assemblies (one-molecule thick) whose spontaneous formation and stability depend

20. J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103.

on favorable intermolecular interactions, and on forces between each individual component molecule and the solid substrate. SAMs are thus organic assemblies formed by the adsorption of suitable molecules from solution or the gas phase onto the surface of metals, metal oxides and semiconductors, either in the solid or in the liquid (e.g. mercury) state. The molecules that form SAMs have a chemical functionality, or "headgroup", with a specific affinity for a substrate. The most popular type of SAM is that formed by the chemisorption of long-chain alkanethiol molecules on clean gold surfaces (see Figure 2.4). The main driving forces for this self-assembly process are: (i) the formation of S–Au bonds (bonding energy estimated to be 40-50 kcal/mol), and (ii) the favourable lateral Van der Waals interactions among the aliphatic chains of neighboring alkanethiol molecules.

These SAMs are prepared simply by exposing a clean gold surface to a solution of the alkanethiol. No special equipment or conditions (e.g., UHV) are required. For alkanethiols with chains longer than 10 carbon atoms, it is generally true that:

i) A stable, organized and densely packed monolayer is readily formed on the Au surface ii) the thickness of the monolayer is directly proportional to the length of the alkanethiol chain. Typical thicknesses range from 1 to 3 nm iii) the main axes of individual molecules are tilted by an angle of ca. 30° from the normal to the surface.
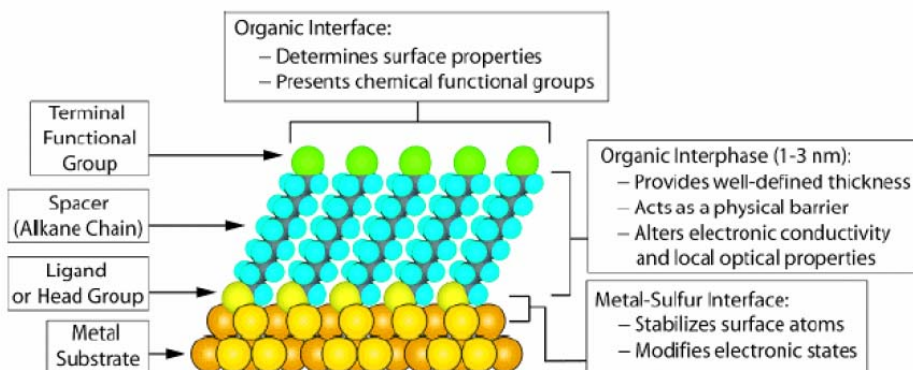
Figure 2.4. Schematic diagram of an ideal single-crystalline SAM of alkanthiolates supported on a gold surface with a (111) texture. The anatomy and characteristics of the SAM are highlighted.

Hybrid materials can be also used to prepare nanomaterials and in particular nanoparticles (solid particles in the 1–1'000 nm range) that present new specific properties which are characteristic of this new physical chemical status.[21] This new topic will be presented in detail in the next paragraph.

2.4 Monolayer protected clusters (MPCs) of gold and other metals

"Monolayer Protected Clusters"[21,22] (MPCs), also known as 3D Self-Assembled Monolayers (3D-SAM),[20] represent an emerging class of organic–inorganic hybrid materials. They are constituted by a discrete

21. A. B. Descalzo, R. Martinez-Màñez, F. Sancenòn, K. Hoffmann, K. Rurack, *Angew. Chem. Int. Ed.* **2006**, *45*, 5924.
22. For a review on monolayer protected clusters see *e.g.*: D. Astruc, M. C. Daniel, *Chem. Rev.* **2004**, *104*, 293.

aggregate of metal atoms (called inorganic core) stabilized by a shell of organic molecules (arranged like a monolayer around the metal surface) that maintain them stable in solution and prevent aggregation effect (see Figure 2.5). The stabilization can be the result either of steric or electrostatic interactions.
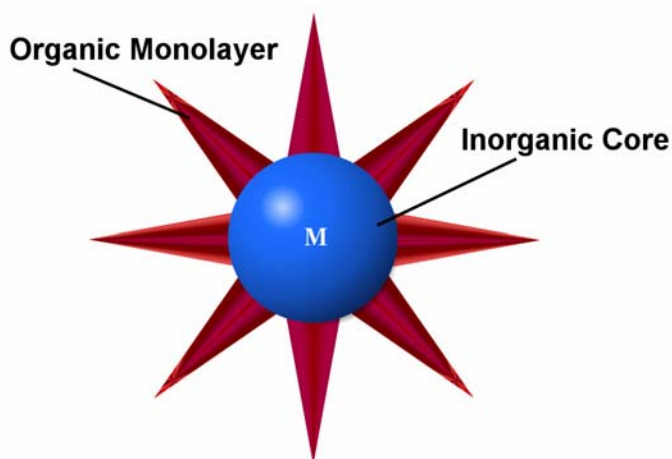

Figure 2.5. Schematic representation of a monolayer protected cluster (MPC)

The properties of these compound strongly depend by the components used to build up both the core and the organic layer. In literature are present several examples of metal MPCs (Ag,[23] Pd,[24] Cu,[25]…) but the most studied are the gold ones (Au MPCs).

The important role assumed nowadays by Au MPCs is, however, strictly derived from the more ancient studies on gold colloids. In the

23. See *e.g.*:A. Brian, A. Korgel, D. Fitzmaurice, *Adv. Mater.* **1998**, *10*, 661 and references therein.
24. See *e.g.*: S. Chen, K. Huang, J. A. Stearns, *Chem. Mater.* **2000**, 540 and references therein.
25. See *e.g.*: T. P. Ang, T. S. A. Wee, W. S. Chin, *J. Phys. Chem. B.* , **2004**, *108*, 11001 and references therein.

latter context, the first study dates back to 1857, when Faraday reported on the formation of deep red solutions of colloidal gold by reduction of an aqueous solution of chloroaurate (AuCl$_4^-$) using phosphorus in CS$_2$ (a two-phase system).[26] In the past decade, Au MPCs have been the subject of a considerably increased number of books[27] and reviews[20,22] especially after the breakthroughs reported by Schmid[28] and Brust et al.[29]

2.4.1 Synthesis of gold nanoparticles and MPCs

Among the conventional methods known for the synthesis of gold nanoparticles through the reduction of Au(III) derivatives, the reduction of HAuCl$_4$ in water by means of sodium citrate has been the most used one. Such a method was introduced by Turkevitch in 1951,[30] and it leads to nanoparticles having a diameter of ca. 20 nm. Modified versions of the Turkevich method found in the literature involve the use of different reducing agents such as ascorbate and the UV Light irradiation.[31] In this way is possible to obtain nanoparticles of particular size and shape (see

26. M. Faraday, *Philos. Trans.* **1857**, *147*, 145.
27. *Nanoparticles – Building blocks for nanotechnology*, Ed.: V. Rotello, Springer, 1st Ed., USA, **2004**.
28. a) G. Schmid, *Chem. Rev.* **1992**, *92*, 1709; b) G. Schmid, L. F. Chi, *Adv. Mater.* **1998**, *10*, 515.
29. a) M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R, Whyman, *J. Chem. Soc., Chem. Commun.* **1994**, 801; b) M. Brust, J. Fink, D. Bethell, D. J. Schiffrin, C. Kiely, *J. Chem. Soc., Chem. Commun.* **1995**, 1655; c) D. Bethell, M. Brust, D. J. Schiffrin, C. Kiely, *J. Electroanal. Chem.* **1996**, *409*, 137.
30. J. Turkevitch, P. C. Stevenson, J. Hillier, *Discuss. Faraday Soc.* **1951**, *11*, 55.
31. J. Kimling, M. Maier, B. Okenve, V. Kotaidis, H. Ballot, A. Plech *J. Phys. Chem. B,* **2006,** *110*, 15700.

Figure 2.6).[32] In this context, in 1973 Frens and co-workers reported an early effort aimed to obtain AuNPs of chosen size by varying the ratio between the reducing/stabilizing agents and gold.[33] This method is very often used even now when a rather loose shell of ligands is required around the gold core in order to prepare a precursor to valuable gold nanoparticles-based materials.
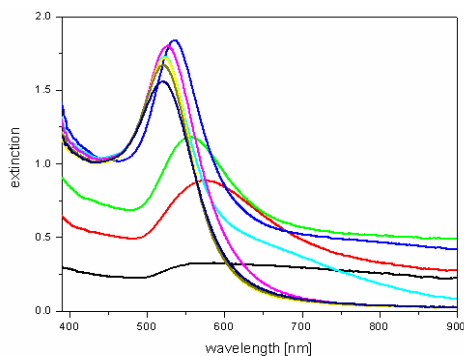
Gold/Citrate	$\frac{1}{0.7}$	$\frac{1}{0.9}$	$\frac{1}{1.1}$	$\frac{1}{1.3}$	$\frac{1}{2}$	$\frac{1}{2.7}$	$\frac{1}{3.3}$	$\frac{1}{4}$	$\frac{1}{6.7}$
λmax	578	575	555	535	522	526	522	520.5	519.3
Diameter	120	110	90	55	21	30	21	19	16

Figure 2.6. Synthesis of different Au MPCs using different amount of citrate. The diameter is expressed in nanometer.[30]

The deep-red colour of the gold sols in water and glasses reflects the surface plasmon band, a broad absorption band in the visible region around 520 nm. The SPB is due to the collective oscillations of the electron gas at the surface of nanoparticles (6s electrons of the conduction band for AuMPCs) that is correlated with the electromagnetic

32. X. Ji, X. Song, J. Li, Y. Bai, W. Yang, X. Peng, *J. Am. Chem. Soc.*, **2007**, *129*, 13939.
33. G. Frens, *Nature: Phys. Sci.* **1973**, *241*, 20.

field of the incoming light, i.e., the excitation of the coherent oscillation of the conduction band (see Figure 2.7).[34]

From the Mie's theory[34] it is possible to determine the average size of the gold nanoparticles through the evaluation of the position of the maximum of the SPB absorption band. Another important aspect of the SPB is that its steepest decrease reflects an high monodispersity of the corresponding nanoparticles. Unfortunately, nanoparticles having mean core diameter lower than 4 nm do not show SPB because of the low "concentration" of electrons at the surface. The solution of such nanoparticles thus appears as black colored.
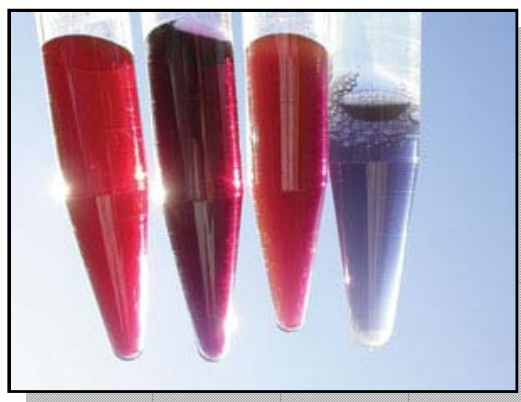

Figure 2.7. Different gold sols in water. The color variation is due to the size of the gold particles.

In 1994 Brust and Schiffrin published a versatile method for the synthesis of Au MPCs covered with alkylthiol chains.[29a] This method allowed, for the first time, the synthesis of thermally stable and air-stable gold clusters of reduced dispersity and controlled size (ranging in diameter between 1.5 and 5.2 nm). Indeed, these clusters could be

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34. G. Mie, *Ann. Phys.* **1908**, *25*, 377.

repeatedly isolated and redissolved in most organic solvents without irreversible aggregation or decomposition. In other words, this new materials could be easily handled and functionalized just as stable organic and molecular compounds.
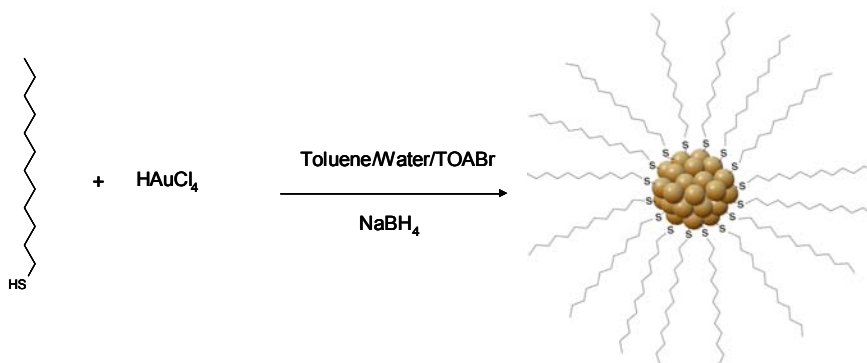

Figure 2.8. Synthesis of Au MPCs with the Brust-Schiffrin method.[29a]

The method of synthesis is inspired by the Faraday's two-phase system[26] and uses thiolated ligands that strongly bind gold due to the "soft" Lewis character of both Au and S. The aurate $AuCl_4^-$ is initially transferred to the toluene phase using tetraoctylammonium bromide as phase-transfer catalyst and reduced in situ by $NaBH_4$, previously dissolved in water, in the presence of dodecanethiol (see Figure 2.8). During this step the organic phase changes its colour from orange to deep brown within a few seconds upon addition of $NaBH_4$ (see Figure 2.9).
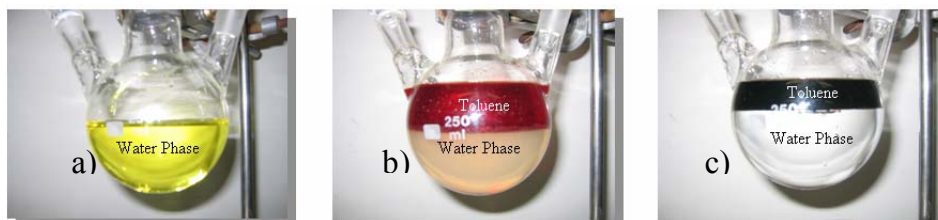
Figure 2.9. Colour changes of the bi-phase system during the synthesis of Au MPCS with the Brust-Schiffrin method: a) before the addition of tetraoctylammonium bromide the water solution containing the aurate (down) is yellow; b) after the addition of tetraoctylammonium bromide the aurate is transferred in toluene (up); after the addition of NaBH$_4$ the organic solution becomes black colored (gold reduction).

The TEM photographs showed that the diameters were in the range 1-3 nm, with a maximum in the particle size distribution at 2.0-2.5 nm, with a preponderance of cuboctahedral and icosahedral structures.

Murray have later shown that large thiol/gold molar ratios give smaller average core sizes. In this paper it has been also demonstrated that fast reductant addition and cooled solutions produced smaller and more monodisperse particles.[35] Several authors have shown that an high abundance of very small clusters (core sizes < 2 nm) is obtained either by quenching the reaction immediately after the gold reduction or by using more bulky ligands.[36]

Brust et al. extended his method of synthesis to a single phase system for the preparation of *p*-mercaptophenol-stabilized Au MPCs.[29b] The single phase system preparation opened an avenue to the synthesis of Au MPCs stabilized by a variety of functional thiol ligands.[37]

35. M. J. Hostetler, J. E. Wingate, C.-J. Zhong, J. E. Harris, R. W. Vachet, M. R. Clark, J. D. Londono, S. J. Green, J. J. Stokes, G. D. Wignall, G. L. Glish, M. D. Porter, N. D. Evans, R. W. Murray, *Langmuir* **1998**, *14*, 17.
36. a) M. J. Hostetler, S. J. Green, Stokes, R. W. Murray, *J. Am. Chem. Soc.* **1996**, *118*, 4212; b) R. S. Ingram, M. J. Hostetler, R. W. Murray, *J. Am. Chem. Soc.* **1997**, *119*, 9175; c) S. Chen, R. W. Murray, *Langmuir* **1999**, *15*, 682; d) S. Chen, *Langmuir* **1999**, *15*, 7551.
37. See *e.g.*: A. C. Templeton, W. P. Wuelfing, R. W. Murray, *Acc. Chem. Res.* **2000**, *33*, 27 and references therein.

Another important reaction that involved Au MPCs is the so-called "place-exchange reaction" of the organic shell developed by Murray and co-workers (see Figure 2.10).[38]
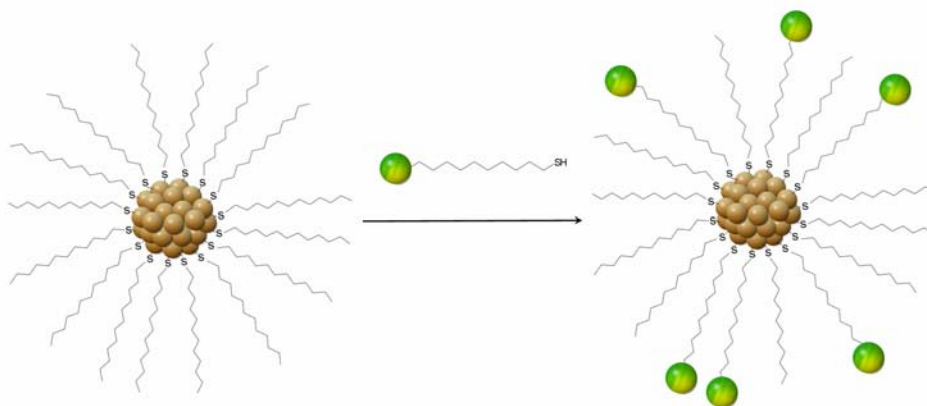

Figure 2.10. Schematic representation of the "place-exchange reaction" involving the organic shell of n-dodecanthiol-stabilized Au MPCs.

This method is very useful for the preparation of Au MPCs coated with an organic shell containing functional groups not compatible with the classic reduction condition (NaBH$_4$), such as aldehyde and ketones. Indeed, the target Au MPCS are synthesized starting from *n*-dodecanthiol stabilized Au MPCs trough exchange with the desired thiolated ligand. The driving force of this process is the large excess of the latter compound. Using this method it is possible to obtain Au MPCs with a great variety of substituents. It is thus possible to synthesize Au MPC characterized by particular and desired chemical properties.

Another type of place-exchange reaction considers as starting material gold clusters stabilized by lipophilic organic salts such tetraalkylammonium salts $R_4N^+X^-$ where R is usually a long alkyl chain

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38. A. C. Templeton, M. J. Hostetler, R. W. Murray, *Langmuir* **1999**, *15*, 3782.

such as butyl or octyl. With this method, developed by Schiffrin in 1998,[39] the gold clusters are prepared as in the classical Brust-Schiffrin procedure, but the addition of the reducing agent is accomplished in absence of the thiolated ligand. In this way, the Au surface of the clusters is stabilized through electrostatic interactions with the anion (Br^-) (see Figure 2.11), while the alkyl chains of the cation are used as surfactant to maintain the particles in solution. This method allows the synthesis of Au clusters having a core size of 3-5 nm and characterized by high monodispersity and stability. The nanoparticles can be then exchanged with whatever thiolated ligands.
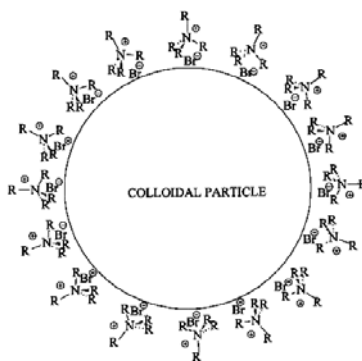

Figure 2.11. Schematic diagram showing the proposed arrangement of R_4N^+ and Br^- species adsorbed on the surface of Au particles.

After the development of these new methods of synthesis, Au MPCs have become an excellent building blocks for nanoscience and nanotechnology.

2.4.2 Investigation tools for the characterization of the MPCs cores

39. J. Fink, C. J. Kiely, D. Bethell, D. J. Schiffrin *Chem. Mater*. **1998,** *10,* 922

The recent emerging of the nanosciences as a new frontier science has been also due by the concomitant development of several new investigation techniques that have helped the scientists to understand the phenomena at nanoscale level. In other words, the progressive ability to fabricate smaller and smaller structures has been followed by an improvement in their characterization.[40] The investigation tools used for the characterization of MPCs range from simple techniques such as elemental analysis and TGA, that allow the determination of the composition of the material, up to more sophisticated ones such as microscopy and photoemission spectroscopy.

High-Resolution Transmission Electron Microscopy (HRTEM): The most common characterization technique for Au MPCs is the (HRTEM),[41] which gives a photograph of the gold core of the AuMPCs.[42] TEM techniques involve a high voltage electron beam emitted by a cathode, usually a tungsten filament and focused by electrostatic and electromagnetic lenses. The electron beam that has been transmitted through a specimen that is in part transparent to electrons carries information about the inner structure of the specimen in the electron beam that reaches the imaging system of the microscope. The spatial variation in this information (the "image") is then magnified by a series of electromagnetic lenses until it is recorded by hitting a

40. C. P. Poole Jr, F. J. Owens, *Introduction to Nanotechnology*, John Wiley & Sons, Hoboken New Jersey, **2003**. ISBN: 0-471-07935-9.
41. D. B. Williams, C. B. Carter, *Transmission Electron Microscopy: A Textbook for Materials Science*, Plenum Press, **1996**.
42. L. Sun, M.R. Crooks, V. Chechik, *Chem. Comm.*, **2001**, 359

fluorescent screen, photographic plate, or light sensitive sensor such as a CCD (charge-coupled device) camera. (see Figure 2.12)

Figure 2.12. A typical TEM istruments

The image detected by the CCD may be displayed in real time on a monitor or computer. Resolution of the TEM is limited primarily by spherical aberration, but a new generation of aberration correctors have been able to partially overcome spherical aberration to increase resolution. Software correction of spherical aberration for HRTEM has allowed the production of images with sufficient resolution to show carbon atoms in diamond separated by only 0.89 Å (89 picometers) and

atoms in silicon at 0.78 Å (78 picometers)[43] at magnifications of 50 million times.

A detailed high-resolution study of the AuMPC shape using HRTEM, revealed that the truncated cuboctahedron predominated (see Figure 2.13)and that decahedra, dodecahedra, icosahedra were also present in the same preparation of alkanetiol-stabilized AuMPCs.
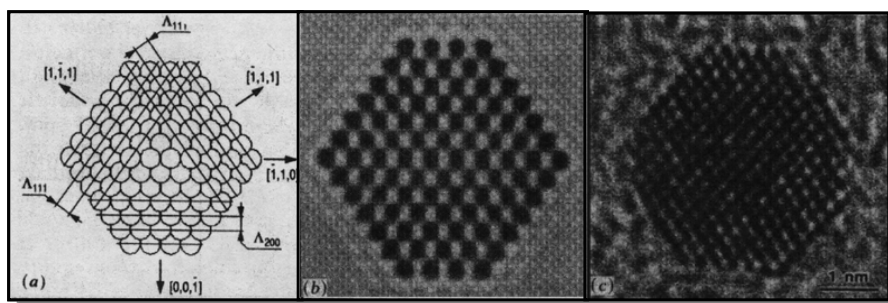

Figure 2.13. a) Schematic representation b) computer simulation and c) HRTEM image of cuboctahedron AuMPCs

The histogram providing the size distribution of these cores gives crucial information on the dispersity of the sample that is usually obtained from TEM pictures. The main diameter, d, of the cores allows determination of the main number of gold atoms, N_{Au}, in the cores: $N_{Au} = 4\pi(d/2)^3/v_{Au}$. For instance, with $d = 2.06$ nm, $N_{Au} = 269$. From these data, the elemental analysis, giving the Au/S ratio, allows calculation of the average number of S ligands. This number can also be deduced from X-ray photoelectron spectroscopy (XPS) or thermo gravimetric analysis (TGA).

43. P. D. Nellist, M. F. Chisholm, N. Dellby, O. L. Krivanek, M. F. Murfitt, Z. S. Szilagyi, A. R. Lupini, A. Borisevich, W. H. Sides, Jr., S. J. Pennycook, *Science*, **2004**, *305*, 1741.

Powder diffraction (XRD):[44] Another method for the characterization of the cluster core is XRD (see Figure 2.14).[45] XRD not only provides definitive identification on the structure but also gives the average size of the cluster core. Evolution of the core structure with decreasing size is observed in XRD patterns. For large clusters, all the peaks are well resolved and, as the size decreases, the reflections become broader.[45a] The size of the particles could be calculated from the X-ray line width broadening using the Scherrer formula for small crystalline spheres:[46]

$$D = \frac{0.9 \cdot \lambda}{B \cdot \cos\theta_B}$$

D = thickness of the crystal in A
λ = X-Ray wavelenght = λ_{cu}=1.5478
θ_B= Bragg angle
$B = \sqrt{B_M^2 - B_S^2}$
B is the peak width at half the peak height

Scherrer Formula

where B_M is the measured peaks and B_S is the correspondence width of a peak of a standard material, mixed in with the sample, whose particle size is considerably grater than 2000 Å and which has a diffraction peak near to the relevant peak of the sample (for example KCl). Powder diffraction has been successfully used for determinations of gold clusters core size.[47]

44. A. Guinier, *X-Ray Diffraction: In Crystals, Imperfect Crystals, and Amorphous Bodies*; Dover Publications, USA, **1994**. ISBN: 0-486-68011-8.
45. a) D. V. Leff, P. C. Ohara, J. R. Heath, W. M. Gelbart, *J. Phys. Chem.* **1995**, *99*, 7036; b) R. L. Whetten, M. N. Shaffigullin, J. T. Khoury, T. G. Schaaf, I. Vezmar, M. M. Alvarez, A. Wilkinson, *Acc. Chem. Res.* **1999**, *32*, 397.
46. A. R. West, *Solid State Chemistry and its Applications*, Wiley, New York, **1987**.
47. C. L. Cleveland, U. Landman, T. G. Schaaff, M. N. Shafigullin, P. W. Stephens, R. L. Whetten, *Phys. Rev. Lett.* **1997**, *79*, 1873.

The core dimensions of Au MPCs can also be determined using other techniques such as small-angle X-ray scattering (SAXS),[48] laser desorption ionisation mass spectrometry (LDI-MS),[49] and nuclear magnetic resonance (NMR) through the measurement of the hydrodynamic radii (diffusion processes) of the clusters.[50]
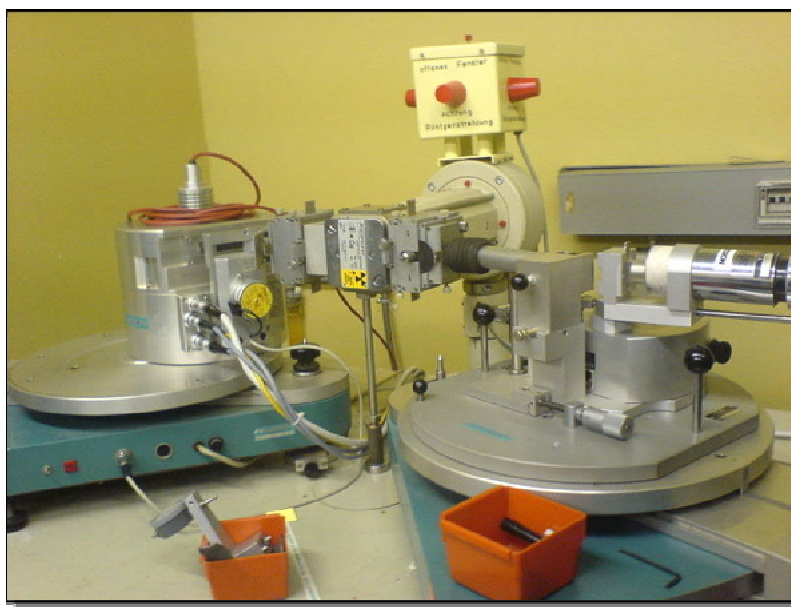

Figure 2.14. A typical XRD instruments

X-ray Photoelectron Spectroscopy (XPS):[51] photoelectron spectroscopic measurements provide information on the chemical state of the constituents of materials. This technique is thus very useful for the

48. B. A. Korgel, D. Fitzmaurice, *Phys. Rev. B* **1999**, *59*, 14191.

49. T. G. Schaaff, M. N. Shaffigulin, J. T. Khoury, I. Vezmar, L.R. Wetten, *J. Phys. Chem. B*, **2001**, *105*, 8785.

50. W. P. Wuelfing, A. C. Templeton, J. F. Hicks, R. W. Murray, *Anal. Chem.* **1999**, *71*, 4069.

51. C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, G. E. Mullenberg, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corp, Eden Prairie, USA, **1979**.

characterization of Au MPCs because XPS spectra for the carbon and sulphur regions are consistent with the presence of alkanethiolate species in the clusters.
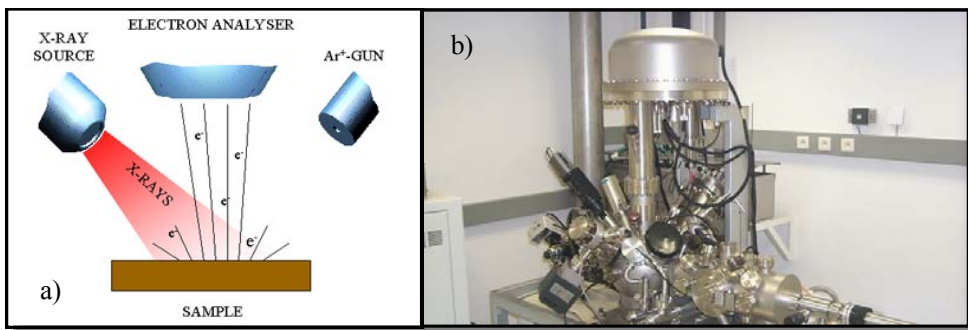

Figure 2.15. a) Schematic rapresentation of a XPS analysis b) A typical XRD instruments

XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy (KE) and number of electrons that escape from the top 1 to 10 nm of the material being analyzed. XPS requires ultra-high vacuum (UHV) conditions (see Figure 2.15). Because the energy of a particular X-ray wavelength correspond to a known quantity, we can determine the electron binding energy (BE) of each of the emitted electrons by using an equation that is based on the work of Ernest Rutherford (1914):

$$E_{binding} = E_{photon} - E_{kinetic} - \Phi$$

where $E_{binding}$ is the energy of the electron emitted from one electron configuration within the atom, E_{photon} is the energy of the X-ray photons being used, $E_{kinetic}$ is the kinetic energy of the emitted electron as

measured by the instrument and Φ is the work function of the spectrometer (not the material).

A typical XPS spectrum is a plot of the number of electrons detected (Y-axis, ordinate) versus the binding energy of the electrons detected (X-axis, abscissa). Each element produces a characteristic set of XPS peaks at characteristic binding energy values that directly identify each element that exist in or on the surface of the material being analyzed. These characteristic peaks correspond to the electron configuration of the electrons within the atoms, e.g., 1s, 2s, 2p, 3s, etc. The number of detected electrons in each of the characteristic peaks is directly related to the amount of element within the area (volume) irradiated. To generate atomic percentage values, each raw XPS signal must be corrected by dividing its signal intensity (number of electrons detected) by a "relative sensitivity factor" (RSF) and normalized over all of the elements detected. To count the number of electrons at each KE value, with the minimum of error, XPS must be performed under ultra-high vacuum (UHV) conditions because electron counting detectors in XPS instruments are typically one meter away from the material irradiated with X-rays. It is important to note that XPS detects only those electrons that have actually escaped into the vacuum of the instrument. The photo-emitted electrons that have escaped into the vacuum of the instrument are those that originated from within the top 10 to 12 nm of the material. All of the deeper photo-emitted electrons, which were generated as the X-rays penetrated 1–5 micrometers of the material, are either recaptured or trapped in various excited states within the material. For most

applications, it is, in effect, a non-destructive technique that measures the surface chemistry of any material.

Brust et al. have examined the oxidation state of the gold atoms of the core in their seminal article using X-ray photoelectron spectra that showed the binding energies of the doublet for Au $4f_{7/2}$ (83.8 eV) and Au $4f_{5/2}$ (87.5 eV) characteristic of Au^0. No band was found for Au^I at 84.9 eV, although one-third of the gold atoms are located at the surface and bonded to thiols for 2.0-2.5 nm sized particle cores.[29a]

2.4.3 Characterization of the monolayer

The structure of alkanethiolate monolayers in MPC has been probed by ^{13}C NMR[52] and transmission IR[53] spectroscopies. ^{13}C NMR focuses on the dependence of chemical shifts as a function of the carbon position relative to the gold–hydrocarbon interface. All the ^{13}C peaks are broadened in the cluster, attributed to the immobilization of the surfactant on the cluster surface. Going from the shorter to longer chain lengths, the peak width narrows, as the carbon is located further away from the thiol functionality. Other significant observations are that the resonances from carbon atoms closest to the Au core, those due to C_α, C_β and C_γ, are broadened into the baseline and that there is a systematic change in both the chemical shift and the line width with the carbon position relative to the Au–hydrocarbon interface. These are attributed to the discontinuity in

52. R. H. Terril, T. A. Postlethwaite, C.-H. Chen, C.-D. Poon, A. Terzis, A. Chen, J. H. Hutchison, M. R. Clark, G. Wignall, J. D. Londono, R. Superfine, M. Falvo, C. S. Johnson, E. T. Samulski Jr, R. W. Murray, *J. Am. Chem. Soc.*, **1995**, *117*, 12537.
53. M. J. Hostetler, J. J. Stokes, R. W. Murray, *Langmuir* **1996**, *12*, 3604.

the diamagnetic susceptibility at the Au–hydrocarbon interface and residual dipolar interactions in alkanethiolate monolayers. Broadening of the resonances as well as the disappearance of the carbons closest to the surface shows the immobilization of the alkyl chains and the strong interaction with the metal surface respectively.

Nevertheless, as it will be reported in the next chapters, we and other research groups did not observe a detectable broadening in the ^{1}H NMR spectra of the nanoparticles studied. The NMR spectra are very informative, as for all molecular compounds, especially for the part of the ligand remote from the core. The latter can also be more fully analyzed, if desired, after oxidative decomplexation using iodine.

IR spectroscopy, shows that, as in 2D SAMs, the thiolate ligands of AuMPCs are essentially in all-trans zigzag conformations, with 5-25% of gauche defects at both inner and terminal locations.[54] IR and NMR spectroscopies allow, together with differential scanning calorimetry (DSC), the detection of order-disorder transitions in AuMPCs in the solid state. The temperature of the transition increases with the chain length, and FTIR can show the increasing amount of gauche defects.

2.5 Hybrid materials and supramolecular chemistry

Functional hybrid systems are based on the attachment of a larger number of a single or several different chemical units on the surface of a metal. From a supramolecular chemistry viewpoint, however, the

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54. T. Ung, M. L. Liz-Marzan, P. Mulvaney, *Colloids Surf. A: Physiochemical. Eng. Asp.,* **2002**, *202*, 119.

functionalization of nanostructured solids with specific groups to enhance active functions, such as the recognition of guests or to switch surface properties, is particularly interesting. Such materials with a high and readily accessible specific surface can amplify certain functional chemical processes. The amplification processes can be principally divided into two classes. One class commonly shows an enhancement of classical recognition features as a consequence of entropic factors associated with the restriction of movement and the proximity of molecular entities on the surface. The second class, often more advanced, does not necessarily recognize a guest much better, but usually provides an amplified output signal that arises from collective phenomena between the preorganized functional units. The step from a one-dimensional molecule to a two-dimensional arrangement—the hetero-supramolecular ensemble—leads to unique properties which are not simply an extrapolation of the solution conduct to the surface.[21]

An examples of combining hybrid materials and supramolecular chemistry is the synthesis of a reversible valve by Stoddart and co workers showed in Figure 2.16.[55]

55. T. D. Nguyen, H.-R. Tseng, P. C. Celestre, A. H. Flood, Y. Liu, J. F. Stoddart, J. I. Zink *PNAS* **2005**, *vol. 102 no. 29*, 10029.
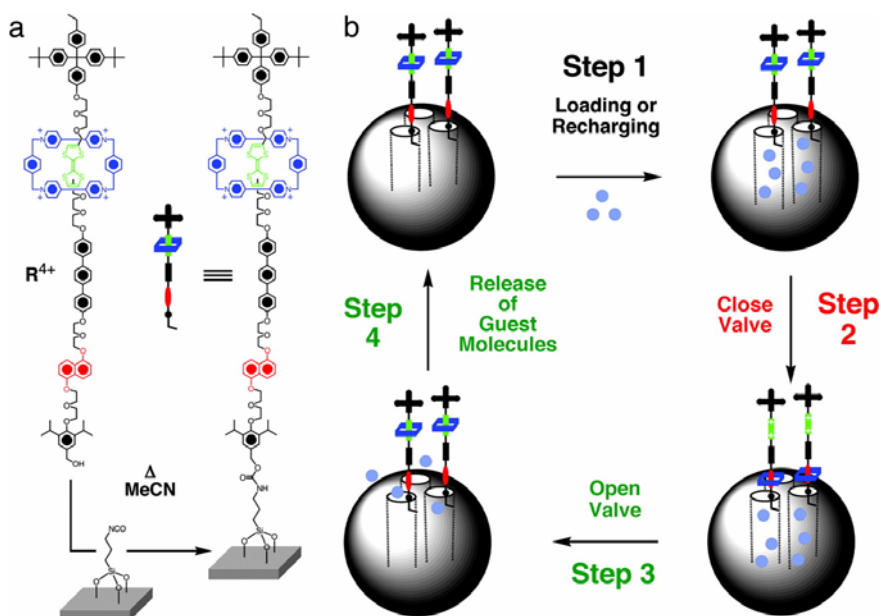
Figure 2.16. Graphical representations of the surface attachment of bistable rotaxanes to silica particles along with a cycle for loading and release of guest molecules. (*a*) The structural formula of the bistable [2]rotaxane R4$^+$ and the procedure used for tethering R4$^+$ to the surface of mesoporous silica particles. (*b*) The proposed mechanism for the operation of the nanovalve. The silica particles are not drawn to scale, and only a few of the ordered pores are shown.

The moving part of the molecular valve is a ring (blue), which shuttles between a station (green) and a another station (red) under redox control. The openings of the cylindrical pores on the silica are blocked by the ring when the valve is closed. Guest molecules (turquoise spheres) are loaded in Step 1 by diffusion into the open pores when the blue ring is located on the green station. The valve is closed in Step 2 by oxidation of the green unit to its dication, causing the blue ring to move to the red station, which is much closer to the openings of the pores. The valve can be opened (Step 3) by adding ascorbic acid to reduce the green dication back to its neutral state, whereupon the ring moves back from the red

station to be relocated around the much more π electron-rich green station, releasing the guest molecules in Step 4. The valve is ready for recharging (i.e., returning to Step 1). Thus, the valve can be closed and opened reversibly.

Another examples consist in the controlled assembly and disassembly of Au MPCs as studied by Reinhoudt and co-workers. Using dendrimers stabilized functionalized with adamantyl units and Au MPCs stabilized by some CD (cyclodextrin) and taking advantage of the strong interaction between cyclodextrin–adamantane they involve the formation of a layer-by-layer structures.[56] CD-functionalized gold or silicon oxide surfaces, adamantyl-terminated dendrimers (5th generation, 64 adamatyl end groups), and gold nanoparticles functionalized with cyclodextrins were the three components used for this multilayer device (see Figure 2.17).
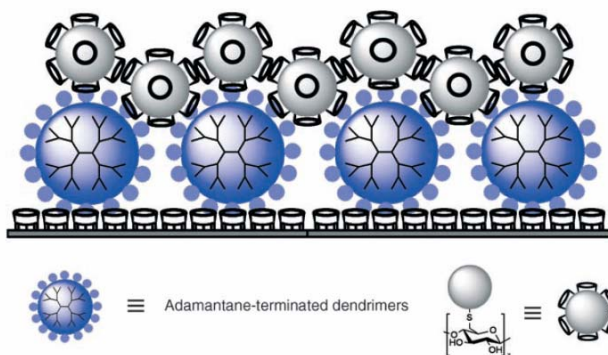

Figure 2.17. Representation of layer-by-layer assembly of adamantly terminated dendrimers and AuMPCs functionalized with cyclodextrins on a CD SAM

56. O. Crespo-Biel, B. Dordi, D. N. Reinhoudt, J. Huskens, *J. Am. Chem. Soc.* **2005**, *127*, 7594

Since small AuMPCs (2.8 nm diameter) were again employed that show negligible shifts of the plasmon band upon aggregation, UV/Vis spectroscopy could be used to monitor the growth of the layers by the increase in the intensity of the plasmon band at 525 nm as a function of the number of bilayers deposited on the surface. Well-defined multilayer thin films with up to 18 nanometer-thick layers were thus created in a controlled manner.