

Chapter 2

Orthogonal Supramolecular Interaction Motifs for Functional Monolayer Architectures

2.1 Introduction

Supramolecular chemistry refers to the area of the chemistry of molecular assemblies and of the intermolecular bond (chemistry beyond the molecule) and focuses on the development of self-assembly pathways toward large molecular systems or molecular arrays [1] Molecular self-assembly has been demonstrated by supramolecular chemistry and can be defined as the spontaneous assembly of the molecules under equilibrium conditions into stable, structurally well-defined aggregates through noncovalent interactions (e.g. hydrogen bonding, metal coordination, electrostatic or host–guest interactions) which are usually weaker than covalent bonds. Moreover, supramolecular interactions are reversible, whereas covalent bonds are usually irreversible. The use of supramolecular interactions to direct the spontaneous assembly of molecules is of utmost importance owing to their high specificity, controlled affinity, and reversibility. These specific and highly controllable interactions can be manipulated independently and simultaneously, providing orthogonal self-assembly which describes the assembly of components with multiple (i.e. more than one) interaction motifs that do not influence each other's assembly properties, applied in the same system [2–6].

Self-assembled monolayers (SAMs) are ordered molecular assemblies formed by the adsorption of an adsorbate onto a solid surface. SAMs provide a convenient way to produce surfaces with specific chemical functionalities. Regarding the concept of controlled positioning of molecules on a surface, binding stoichiometry, binding strength, binding dynamics, packing density and order, and reversibility serve as crucial tuning parameters. Covalent immobilization of molecules does not offer convenient versatility and flexibility over most of these parameters. Supramolecular interactions afford a solution to the control of these criteria. Hence, the orthogonal self-assembly concept, integrated with various surface patterning methods such as soft-lithography, provides rapid and site-selective adsorption of

molecules and micrometer scale objects at predefined regions with high specificity and selectivity for the fabrication of complex hybri organic–inorganic materials.

Comprehensive reviews exist on orthogonal supramolecular interactions in solution [7, 8]. Objective of this chapter is to give an overview of the current understanding of orthogonal supramolecular interactions and its potential as a self-assembly tool on solid surfaces. For this reason, the focus will be on the individual supramolecular interaction motifs (hydrogen bonding, metal coordination, electrostatic and host–guest interactions) as well as recent advances for the combination of these orthogonal interactions for functional monolayer architectures on surfaces.

2.2 Hydrogen Bonding Directed Assembly on Surfaces

Self-assembly through multiple hydrogen bonding interactions has been widely used to create functional monolayers and new materials on surfaces. Multiple hydrogen bonding is of major importance in order to the enhanced stability of systems and allows assembly at near-equilibrium conditions, which facilitates control over the thermodynamic parameters of the assembly.

2.2.1 *Assembly of Molecules on SAMs*

Rotello and coworkers have developed a method to manipulate conductance using hydrogen bonding interactions at a self-assembled monolayer surface (Fig. 2.1) [9]. A binder molecule, diacyl 2, 6-diaminopyridine decanethiolate, was inserted into a background monolayer of decanethiolate on gold using replacement lithography. Electroactive functionalization of the monolayer was then achieved through binding of the complementary ferrocene-terminated uracil to the binder molecule. The ferrocene functionality can be replaced by dodecyl uracil for erasing the conductance. Current–voltage properties of the patterned region were monitored by using an STM tip. Noncovalent self-assembly provides a potential method to install and subsequently remove electroactive functionality.

Rotello and coworkers used three-point hydrogen bonding interactions between modified SAMs and complementary functionalized mono- and di- block copolymers to direct the adsorption process onto surfaces [10]. The thymine-diamidopyridine (Thy-DAP) hydrogen bonding motif provided a highly selective adsorption of the DAP- containing mono- and di- block copolymers onto the Thy-decorated gold surface under controlled deposition conditions (Fig. 2.2).

The group of Cooke demonstrated that phenanthrenequinone binds strongly to ureas and thioureas by forming two hydrogen bonds which can be modulated by altering the redox state of the quinone [11]. A SAM of a disulfide phenanthrenequinone binds phenyl urea-terminated PPI dendrimers by forming multiple

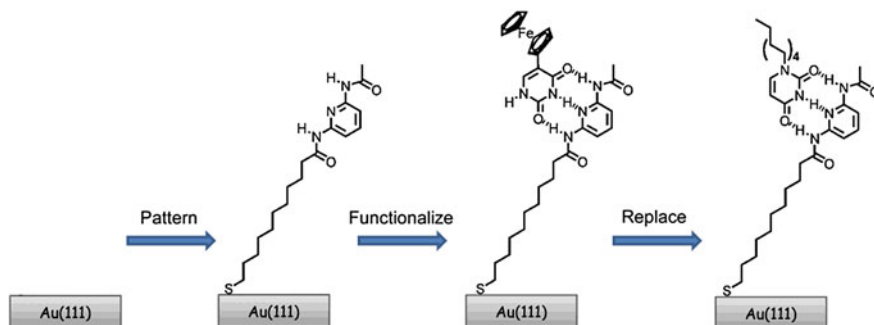


Fig. 2.1 Patterning, functionalization, and erasing at the surface of assembled monolayer. Adapted with permission from Ref. [9]. Copyright 2002 American Chemical Society

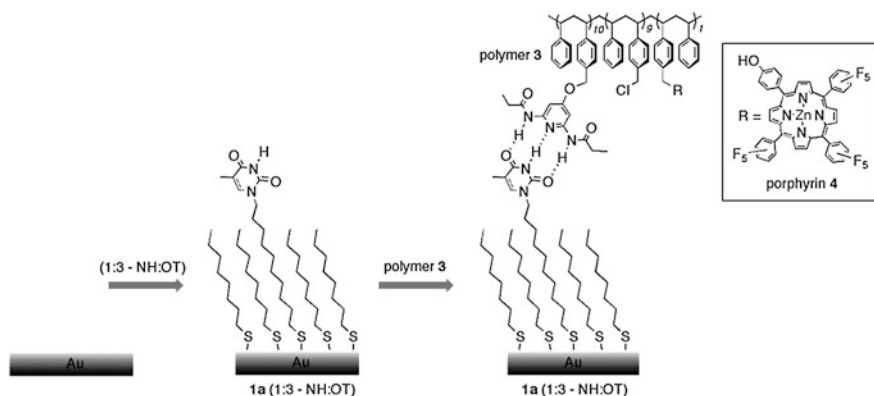


Fig. 2.2 Polymers tethered to surfaces using hydrogen bonding interactions. Adapted with permission from Ref. [10]. Copyright 2003 American Chemical Society

interactions. Upon oxidation, the dendrimers bind to the surface 2000-fold stronger while for a monovalent model compound a smaller increase of binding strength was observed. Myles and coworkers have described the immobilization of barbituric acid derivatives on mixed monolayers of alkanethiols and bis(2,6-diaminopyridine) amide of isophthalic acid-functionalized dedecanethiol on gold films [12]. The immobilization of barbiturate derivatives to the receptor-functionalized SAM involved the use of multiple hydrogen bonds to achieve a stable assembly on the surface (Fig. 2.3).

Reinhoudt et al. have reported synthetic hydrogen-bonded assemblies on gold surfaces [13]. The spontaneous assembly process was performed by incorporating the thioether-functionalized calix[4]arene dimelamines into a thiolate SAM. Subsequently, the monolayers containing one of the building blocks were immersed in a solution of the already formed assemblies, resulting in stable hydrogen-bonded assemblies at the surface (Fig. 2.4).

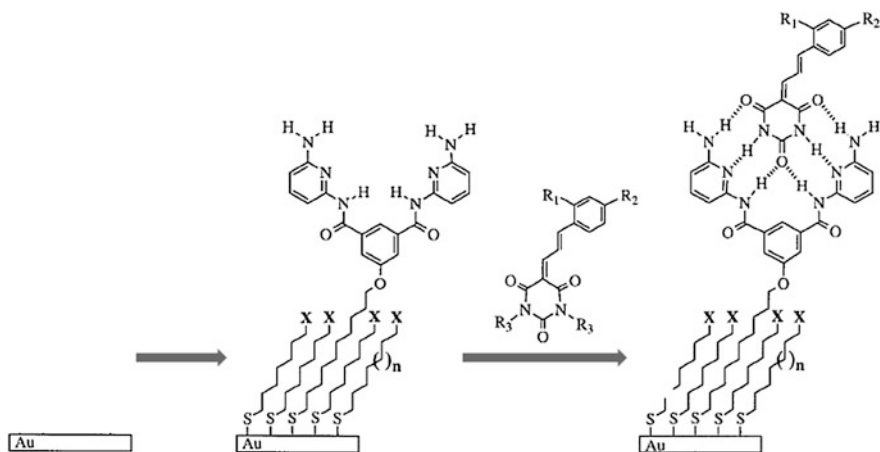


Fig. 2.3 Assembly between barbituric acid derivatives and the bis(2, 6-diaminopyridine) amide of isophthalic acid on a gold film. Adapted with permission from Ref. [12]. Copyright 1998 American Chemical Society

2.2.2 Assembly of Nanoparticles on SAMs

Binder and coworkers described an example of hydrogen bonding interaction for nanoparticle assembly on flat surfaces [14]. The approach is based on the multiple hydrogen bonding interactions of the receptor immobilized on nanoparticles. It was found that the surface coverage of nanoparticles could be adjusted by the density of receptor units in the mixed SAM (Fig. 2.5).

Rotello and coworkers developed nanoparticle assembly on flat surfaces through specific hydrogen bonding interactions [15]. They demonstrated the selective deposition of polystyrene functionalized with complementary diamidopyridine (PS-DAP)/and thymine (PSThy) gels onto prepatterned silicon substrates. These microgel arrays can be cross-linked and selectively and reversibly functionalized by nanoparticles through complementary hydrogen bonding interactions to provide polymer/nanoparticle composite microstructure patterns with fluorescent or magnetic properties.

The same group reported the use of electron-beam lithography (EBL) to pattern a functional polymer “host” template composed of diaminotriazine-functionalized polystyrene via electron-beam-induced cross-linking [16]. After development, the cross-linked polymer pattern provides templates for assembling complementary thymine-functionalized CdSe-ZnS quantum dots (QDs) via three point hydrogen bonding interactions.

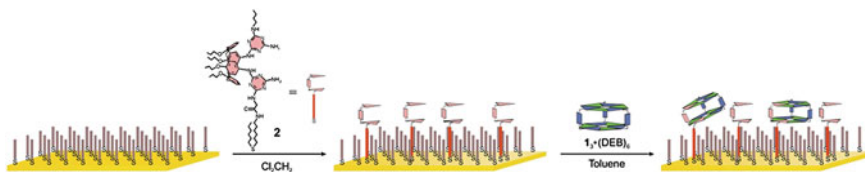


Fig. 2.4 The methodology followed for the growth of assemblies $1_2.2.(DEB)_6$ on gold. Reproduced with permission from Ref. [13]. Copyright 2003 The Royal Society of Chemistry

2.3 Metal Coordination Directed Assembly

Metal-directed self-assembly on surfaces has been extensively studied for the construction of supramolecular architectures. Coordination chemistry is of special interest for the assembly, because it offers stable bonding and metal–ligand specificity, also allows the reversible formation and cleavage of the complex by redox processes or the addition of competing ligands.

2.3.1 Assembly of Molecules on SAMs

Abruna et al. have reported ligand–metal assembly on gold for the preparation of redox active mono- and multimetallic systems [17]. Study shows that the surface-bound terpyridine ligand has enough coordination sites to bind other metal ions on the surface (Fig. 2.6a). A similar approach was used by Nishihara and coworkers to build polymetallic complexes on gold by repetitive deposition of an Fe(II) complex with azobenzene-linked bis(terpyridine) ligand [18]. The group of Schubert described the use of a terpyridine–metal complex to reversibly functionalize surfaces [19]. The optical surface properties could be tuned by the choice of the coordinating metal ion. The introduction of suitable coordinating transition metal ions allowed the reversible formation and disassembly of the surface bounded complexes (Fig. 2.6b). Reinhoudt and coworkers used the metal coordination to generate coordination cages directly on surfaces by using self-assembly [20]. Metal-induced coordination allowed the direct measurement of the formation of such assemblies and detection on a single molecule level. The same group also developed a new way to immobilize heterocages on surface by metal coordination [21]. Immobilized heterocages result from the insertion of the thioether-functionalized cavitand into an 11-mercapto undecanol SAM, followed by assembly of cages by complexation of a different cavitand from solution. A different approach for the metal coordination directed assembly was developed by Rubinstein and coworkers [22]. Using bishydroxamate ligands and corresponding metals such as Zr^{4+} , Ce^{4+} and Ti^{4+} , a new type of multilayer structures based on supramolecular metal–ligand interactions has been constructed in a step-by-step manner, resulting

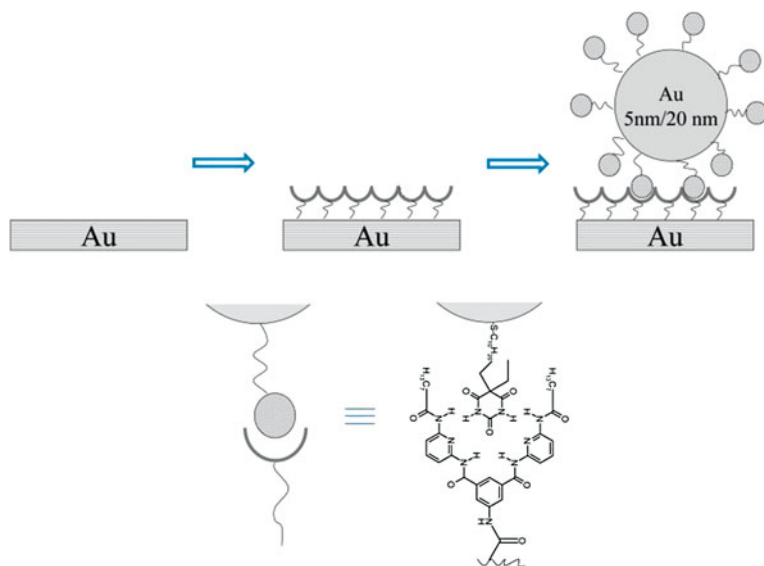


Fig. 2.5 Schematic illustration of hydrogen bonding-directed nanoparticle assembly. Adapted with permission from Ref. 14. Copyright 2005 American Chemical Society

in larger thickness, increased roughness, higher electrical resistivity, and improved stiffness of surfaces (Fig. 2.7).

Mallouk and coworkers used similar type tetravalent (Zr^{4+} , Hf^{4+}) or divalent (Zn^{2+} , Cu^{2+}) metal ions and phosphonates as a ligand to build up multilayers in a supramolecular metal–ligand coordination manner [23]. Papadimitrakopoulos et al. demonstrated the stepwise self-assembly process of diethyl zinc and bis-quinoline on a silicon substrate resulting in films capable of electroluminescence. Assembled films also showed a high refractive index and uniformity [24]. McGimpsey and coworkers developed a non-covalent metal–ligand coordination for the assembly of supramolecular photocurrent-generating systems [25]. In their system, the light absorbing group (pyrene) was noncovalently coupled to a gold surface via metal–ligand complexation. These systems were noncovalently assembled by sequential deposition of three or more components, showing high stability and high current generation on gold surface.

2.3.2 Assembly of Nanoparticles on SAMs

Murray et al. developed a new way to fabricate monolayer or multilayer films of carboxylate-functionalized gold nanoparticles onto a mercaptoundecanoic acid monolayer [26–29]. Nanoparticles were attached via divalent metal ions (Cu^{2+} , Zn^{2+} , Pb^{2+}). Attachment of additional layers of particles was performed by

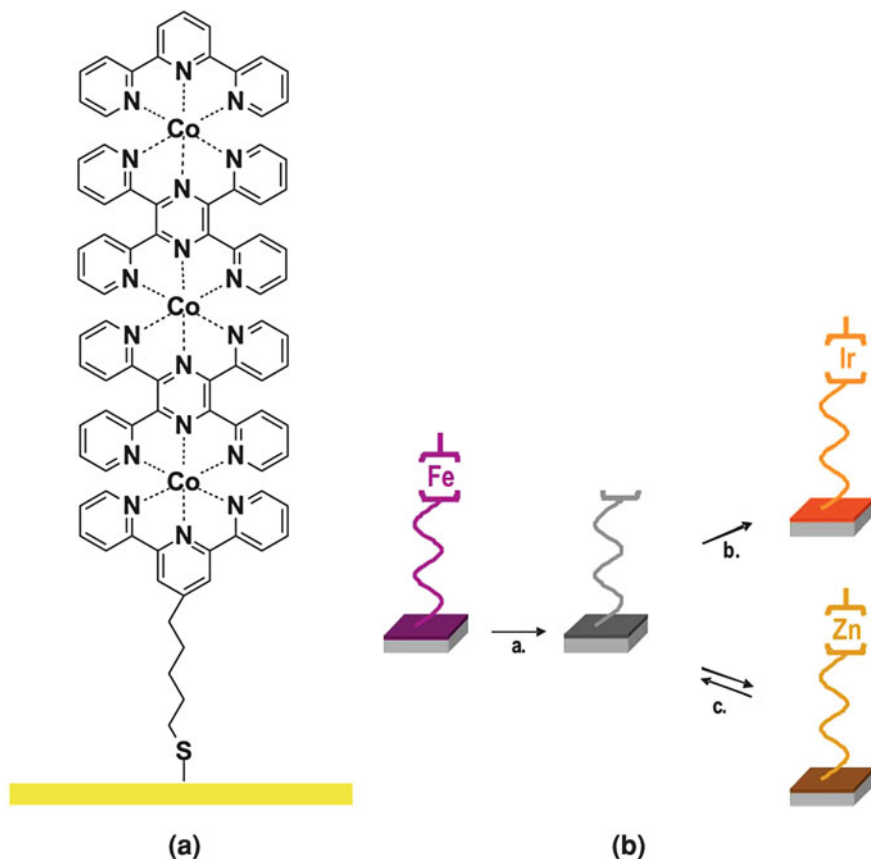


Fig. 2.6 **a** Orthogonal assembly scheme for the construction of terpyridine-metal complex layer on gold. Adapted with permission from Ref. 17. Copyright 1996 American Chemical Society. **b** The attached Fe(II) complex was uncomplexed to obtain the free terpyridine ligands on the substrates *a*. these units can be used for the subsequent complexation with an iridium precursor *b* or with Zn(II) ions; the latter system can be reversibly opened and closed *c*. Reproduced with permission from Ref. [19]. Copyright 2008 American Chemical Society

repeated dipping cycles of metal ions and particles, resulting in the formation of network nanoparticle films. The group of Rubinstein reported gold nanoparticle mono- and multilayers on gold surfaces using coordination chemistry [30]. Au nanoparticles capped with a monolayer of 6-mercaptohexanol were modified by partial substitution of bishydroxamic acid disulfide ligand molecules into their capping layer. A monolayer of the ligand-modified Au nanoparticles was assembled via coordination with Zr^{4+} ions onto a gold substrate precoated with a self-assembled monolayer of the bishydroxamate disulfide ligand. Layer-by-layer construction of nanoparticle multilayers was achieved by alternate binding of Zr^{4+} ions and ligand-modified nanoparticles onto the first nanoparticle layer (Fig. 2.8).

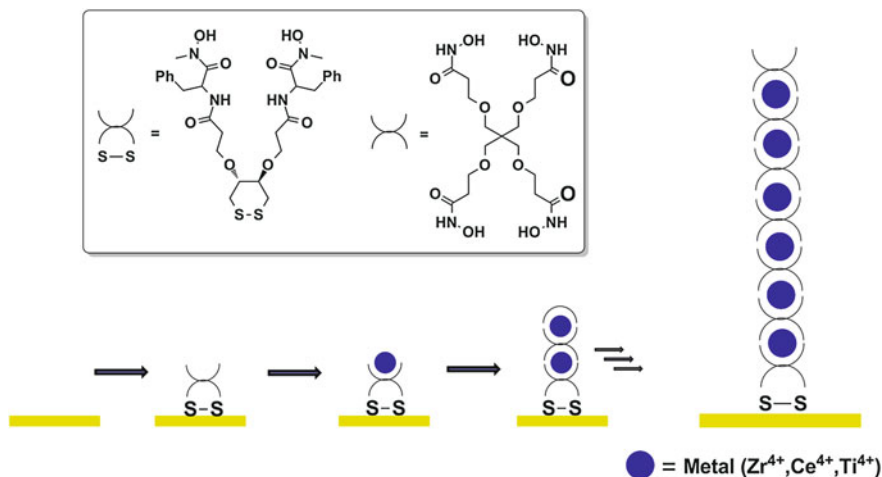


Fig. 2.7 Schematic presentation of the molecules used for multilayer construction and an idealized structure of the coordination-based multilayers. Adapted with permission from Ref. [22]. Copyright 2004 American Chemical Society

Chen and coworkers used metal–ligand coordination (divalent metal ions and pyridine moieties as a ligand) for the assembly of nanoparticles on surfaces [31]. The thickness of the nanoparticle layers was controlled by repetitive alternate dipping cycles (Fig. 2.9).

Reinhoudt et al. used coordination chemistry to grow isolated nanoparticles on surfaces [32]. Pd^{2+} -containing pincer adsorbate molecules were embedded into mercaptoundecanol and decanethiol SAMs on gold. Monolayer-protected Au nanoclusters bearing phosphine moieties at the periphery were coordinated to SAMs containing individual Pd^{2+} pincer molecules via supramolecular metal–ligand interactions.

2.3.3 Assembly by Electrostatic Interactions

One of the most simple and versatile methods for the assembly of 2D and 3D structures is electrostatic self-assembly. The driving force for the assembly is the ionic interaction between oppositely charged entities (polymers, nanoparticles, and substrates), providing the fabrication of functional mono- or multilayer architectures in a stepwise fashion. Electrostatic self-assembly has been the most widely used method for the assembly of the different materials on surfaces. Electrostatic forces are strong enough to create stable assemblies, but weak enough to respond to environmental changes such as variations of ionic strength or pH.

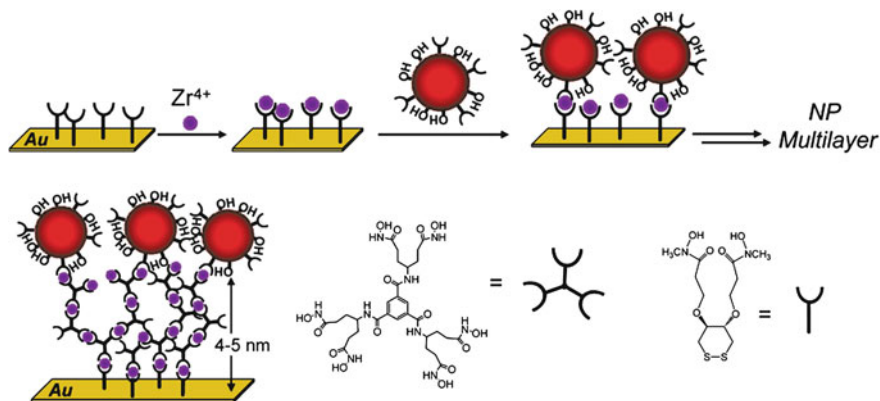


Fig. 2.8 Stepwise assembly of bishydroxamate-bearing Au nanoparticle multilayers onto bishydroxamate disulfide SAMs on a gold surface via Zr^{4+} ions (*top*). Controlled spacing of nanoparticles from the gold surface using a hexahydroxamate ligand (*bottom*). Reproduced with permission from Ref. [30]. Copyright 2005 American Chemical Society

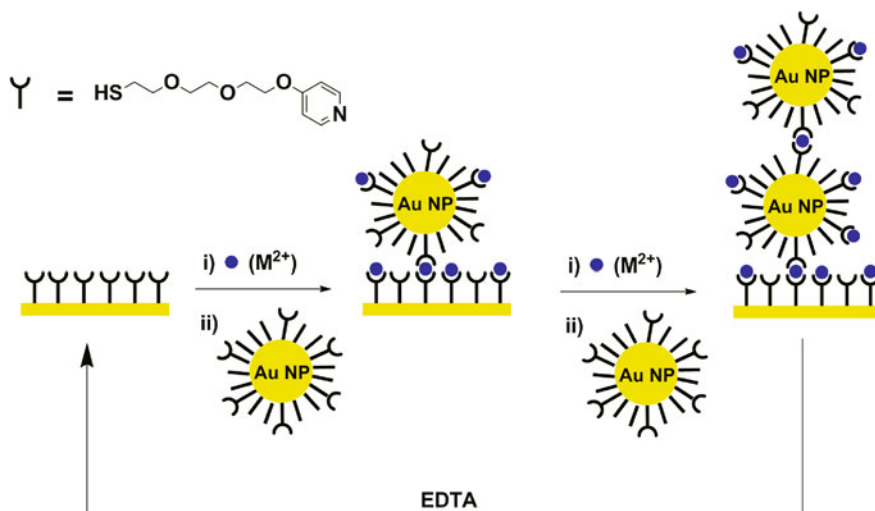


Fig. 2.9 Procedure for nanoparticle assembly by the chelating interactions between divalent (transition) metal ions and pyridine moieties. Adapted with permission from Ref. [31]. Copyright 2002 American Chemical Society

2.3.4 Assembly of Molecules on SAMs

The group of Reinhoudt used electrostatic self-interactions to prepare SAMs of organic radicals on silicon substrates [33]. For this purpose, amino groups on surface were protonated by rinsing with a 4-morpholineethanesulfonic acid

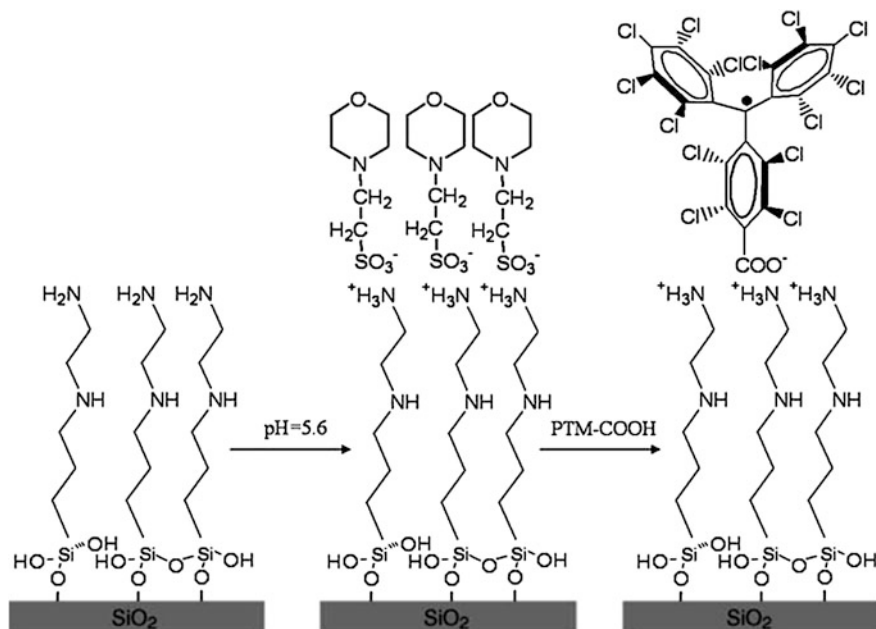


Fig. 2.10 Formation of the polychlorotriphenylmethyl (PTM) radical SAMs on a SiO₂ surface by electrostatic interaction. Reproduced with permission from Ref. [33]. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA

monohydrate buffer (pH 5.6) to give a positively charged surface and, subsequently, the substrate was immersed in a solution of 4-carboxytetradecachlorotriphenylmethyl radical (PTMCOOH) to give a SAM of the organic radical (Fig. 2.10). Calvo and coworkers reported the assembly of some enzymes such as glucose and lactate oxidases on gold by electrostatic adsorption [34]. A polycation, poly (allylamine), was assembled onto a gold electrode modified with 3-mercaptopropane-sulfonic acid by electrostatic interaction. Enzymes were also immobilized onto the polycation layer electrostatically.

An approach for the construction of photoactive devices is highly ordered immobilization of photofunctional molecules on surfaces. For that purpose, Tamiaki et al. reported the electrostatic layer-by-layer adsorption of the light-harvesting complexes (chlorosomes) from the green sulfur photosynthetic bacterium *Chlorobium (Chl.) tepidum* onto a glass substrate using the cationic linear polymer polylysine [35]. Burgin and coworkers examined the electrostatic nature of single-walled carbon nanotubes (SWNTs) adsorption on amine surfaces via electrostatic interactions, where both the amine and the SWNTs were treated by various pH buffers prior to solution deposition of nanotubes [36]. In a similar manner, Bao et al. fabricated amine silane SAMs with varying end groups that led to adsorption of submonolayer nanotube network films with varying degrees of

alignment and density [37]. The protonation of amine-coated surfaces influences this adsorption and chirality sorting of SWNTs (Fig. 2.11).

Ionic interactions have also been used for nanoparticle assembly on surfaces. For instance, Auer and coworkers studied the assembly of gold nanoparticles on planar gold surfaces precoated with mercaptohexadecanoic acid using bisbenzamidines as a linker between negatively charged gold nanoparticles and the surface [38]. Murphy and coworkers used gold nanorods to assemble on a surface by electrostatic interaction [39]. Gold nanorods were stabilized with cetyltrimethylammonium bromide (CTAB) and assembled on a gold surface modified with 16-mercaptohexadecanoic acid. Attractive electrostatic interactions between the carboxylic acid group on the SAM and the positively charged CTAB molecules are likely responsible for the nanorod immobilization (Fig. 2.12).

A similar approach was used by Sastry and coworkers [40]. They described the formation of self-assembled monolayers (SAMs) of an aromatic bifunctional molecule, 4-aminothiophenol (4-ATP) on gold and the subsequent organization of carboxylic acid derivatized silver colloidal particles.

The controlled organization and precise positioning of nanoparticles on 2D surfaces are essential for the development of new functional materials. Some studies focused on the combination of top-down surface patterning with self-assembly of particles via electrostatic interactions. For example, patterning by photolithography [41–43], soft lithography [44, 45], nanoimprint lithography [46], and scanning probe lithography [47–55] have been widely used for the fabrication of electrostatically assembled nanoparticles on patterned surfaces.

2.3.5 Assembly by Host–Guest Interactions

Host–guest chemistry plays an important role in the construction of supramolecular architectures on surfaces. Calixarenes, cucurbiturils (CB), and cyclodextrins (CD) are interesting host molecules which form stable and specific inclusion complexes with a variety of organic guest molecules. Monolayers of these host molecules on surfaces constitute the unique platforms for the immobilization of various guest molecules in a multivalent supramolecular fashion. This section describes the supramolecular assembly onto different receptor surfaces by host–guest interactions.

2.3.6 Assembly of Molecules on SAMs

Calixarene monolayers have been synthesized and characterized extensively by the group of Reinhoudt [56–58]. Calixarenes formed well-packed and ordered monolayers capable of interacting with different guest molecules in aqueous solution. Gupta and coworkers showed that calix[4]arene monolayers could discriminate

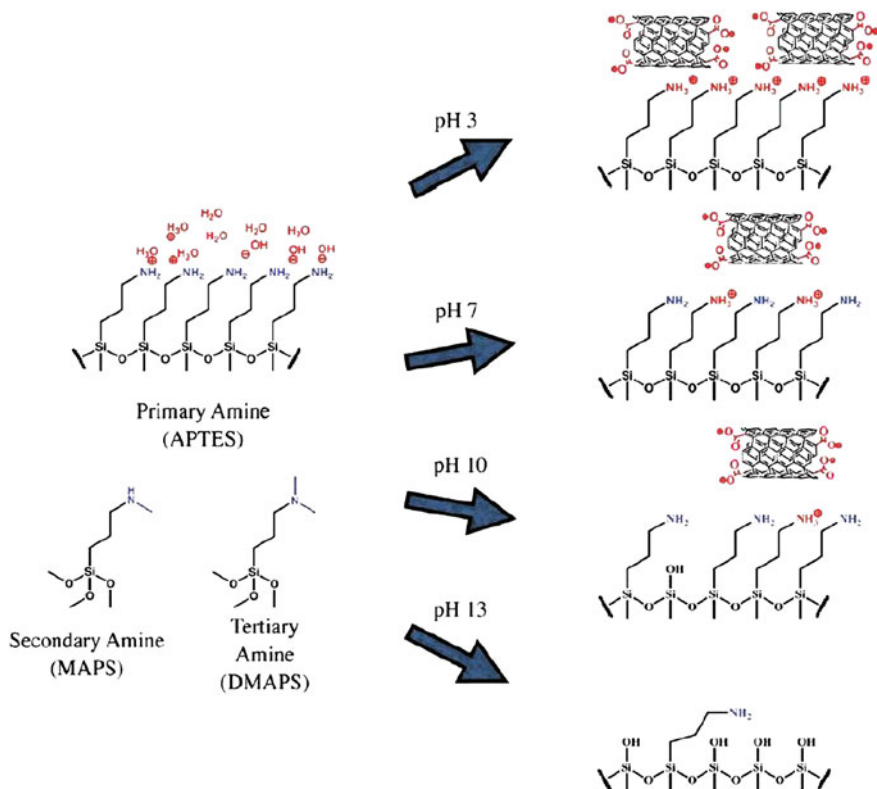


Fig. 2.11 Schematic illustration of influence of protonation on SWNTs adsorption. Reproduced with permission from ref [29]. Copyright 2010 American Chemical Society

between two structural isomers of hydroxybutyrolactone by surface immobilization of the receptor units [59].

Monolayers of cucurbit[6]uril, a macrocyclic cavitand comprising six glycoluril units, have been described by Kim and coworkers [60]. Alkene functionalized CB[6] was reacted with surface-immobilized thiols under UV light, resulting in CB[6] monolayers on a glass surface. The CB[6] modified glass recognizes small molecules such as spermine which is known to form a stable host–guest complex with CB[6] (Fig. 2.13).

Zhang et al. described a general protocol based on the spontaneous adsorption of cucurbit[n]uril (CB[n]) molecules through a strong multivalent interaction between CB[n] and gold [61]. Their method does not require any prior modification or special treatment of CB[n] molecules, and is applicable for all members of the CB[n] family, at least CB[6–8] (Fig. 2.14).

Jonkheijm and coworkers also used a CB[7] monolayer for the immobilization of the proteins through a monovalent supramolecular interaction [62]. Their technique allows printing of stable protein monolayers in well-defined formats to

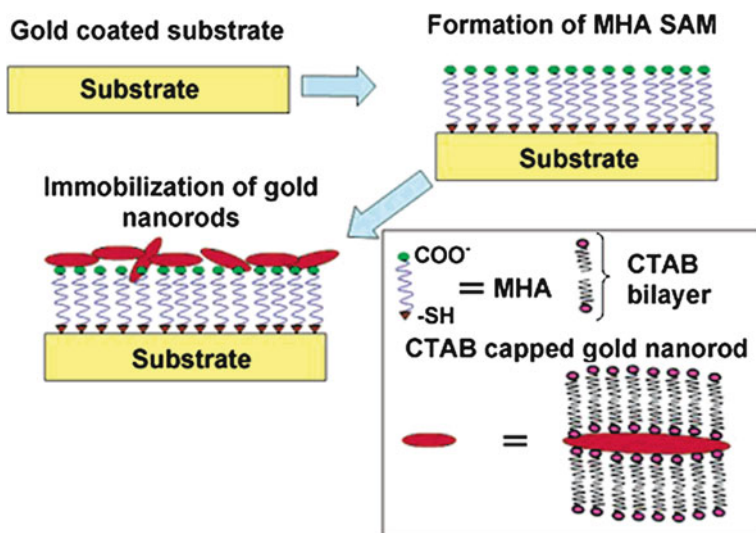


Fig. 2.12 Schematic immobilization of CTAB-Modified Gold Nanorods onto SAMs of 16-MHA. Reproduced with permission from Ref. [39]. Copyright 2004 American Chemical Society

be achieved with controlled protein orientation and with subsequent replacement of the protein monolayer by a small synthetic ligand (Fig. 2.15).

Monolayers of cyclodextrin (CD SAMs) have been studied and extensively characterized. The immobilization of a wide range of (bio)molecules functionalized with multiple guest units onto CD SAMs on gold and silicon oxide surfaces have been reported by different research groups (Fig. 2.16) [63–67]. Huskens and Reinhoudt et al. introduced the concept of “molecular printboards”, for the stable positioning and assembly of guest-functionalized dendrimers [68], nanoparticles [69], proteins [70], and fluorescent small molecules [71] onto CD SAMs. Molecular patterns of (bio)molecules have also been prepared on these molecular printboards by using lithographic techniques such as microcontact printing and dip-pen nanolithography [46, 72–74].

2.4 Combination of Different Orthogonal Supramolecular Interaction Motifs

All supramolecular interactions reviewed here, i.e., hydrogen bonding, metal–ligand coordination, electrostatic, and host–guest interactions, have in common a high level of structural definition and tunable strength, which allow the design of functional materials at the molecular level. As discussed above, these weak

Fig. 2.13 Cartoon for anchoring a CB[6] derivative onto a patterned glass and detection of fluorescently labeled spermine by the CB[6] modified surface. Reproduced with permission from Ref. [60]. Copyright 2003 American Chemical Society

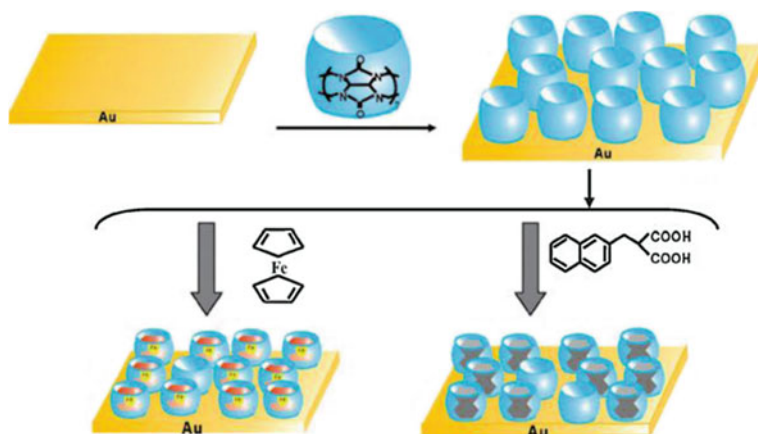
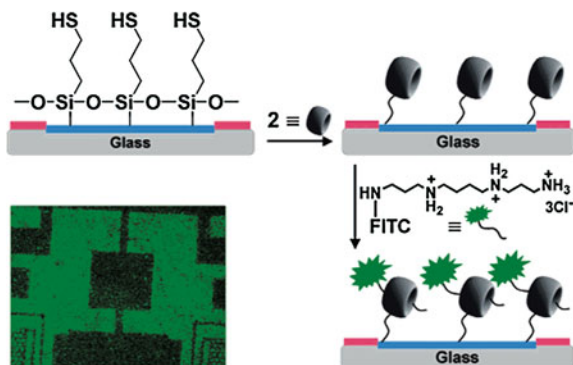


Fig. 2.14 Schematic illustration of the construction of a self-assembled CB[n] monolayer on a gold surface and the formation of inclusion complexes. Reproduced with permission from Ref. [61]. Copyright 2008 The Royal Society of Chemistry

interactions were employed individually to build functional supramolecular architectures on surfaces. The combination of different orthogonal supramolecular interaction motifs is essential for the fabrication of complex hybrid organic–inorganic materials and stimuli-responsive surfaces. This section highlights the recent developments of the combination of different orthogonal interaction motifs to yield hierarchical supramolecular assemblies on surfaces.

Huskens et al. have described the combination of different orthogonal supramolecular systems on molecular printboards. In a first study, they demonstrated the immobilization of a supramolecular capsule at the surface [75]. Two different orthogonal systems, host–guest and electrostatic interactions, were utilized to generate a capsule on a surface. To build such a supramolecular capsule, they used noncovalent attachment of one component of the molecular capsule on the CD SAM via orthogonal host–guest interaction followed by the self-assembly of the

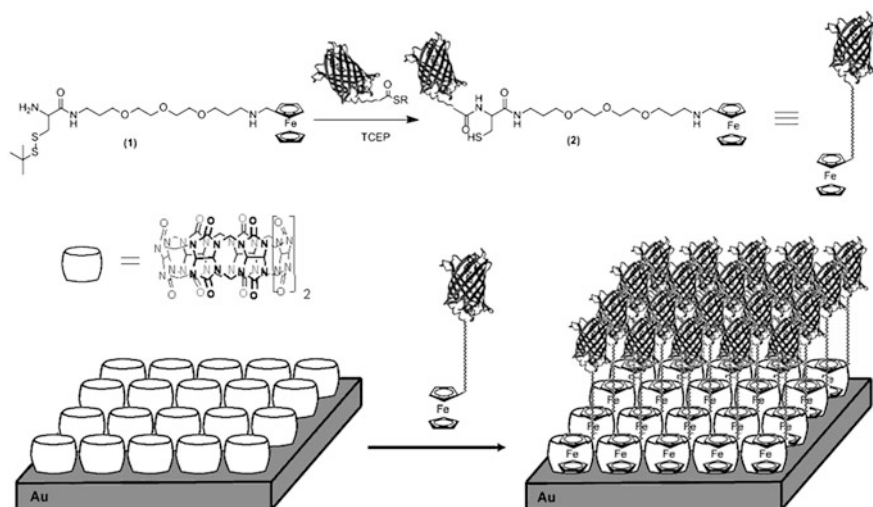


Fig. 2.15 Ligation of a ferrocene-cysteine derivative (1) with yellow fluorescent protein (YFP) and immobilization of the resulting ferrocene-YFP (2) onto a CB[7] monolayer. Reproduced with permission from Ref. [62]. Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA

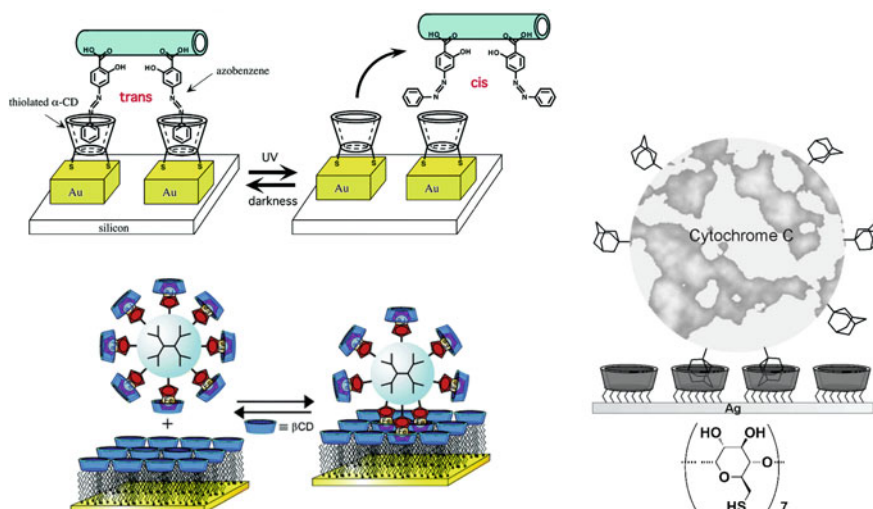


Fig. 2.16 Supramolecular interaction motifs at CD SAMs. Reproduced with permission from Ref. 64 (Copyright 2003 American Chemical Society), Ref. 66 (Copyright 2002 American Chemical Society), Ref. 67 (Copyright 2004 American Chemical Society)

second component at the interface through ionic interaction (Fig. 2.17a). Another study describes the multivalent binding of a supramolecular complex at a multivalent host surface by combining the orthogonal CD host-guest and metal ion-

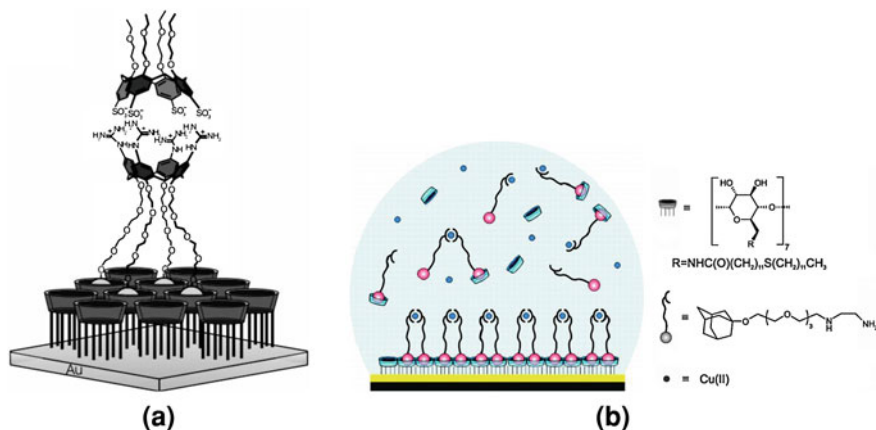


Fig. 2.17 **a** Formation of molecular capsule at CD SAMs via host–guest and electrostatic interactions. Reproduced with permission from Ref. 75. Copyright 2004 American Chemical Society. **b** Complex formation on CD SAMs by host–guest and metal–ligand coordination. Reproduced with permission from Ref. [76]. Copyright 2006 American Chemical Society

ethylenediamine coordination motifs [76]. In this orthogonal supramolecular system, a heterotropic divalent linker, with a CD-complexing adamantyl (Ad) group and an M(II)-complexing ethylenediamine ligand, is employed. This allows the linker to bind to CD in solution as well as to CD immobilized at SAMs (Fig. 2.17b). A similar study describes the preparation of vesicles bearing host units (cyclodextrin) and their interactions with guest (adamantyl) functionalized ligands via orthogonal multivalent host–guest and metal–ligand complexation [77]. Vesicles of amphiphilic cyclodextrin recognized metal coordination complexes with adamantyl ligands via inclusion in the host cavities at the vesicle surface. In the case of divalent Cu(II) complexes, the interaction was predominantly intravesicular. In the case of Ni(II), the interaction was effectively intervesicular, and addition of the guest–metal complex resulted in aggregation of the vesicles into dense, multilamellar clusters. The valency of molecular recognition at the surface of vesicles and the balance between intravesicular and intervesicular interaction could be tuned by metal coordination of guest molecules. Another study, they presented the attachment of streptavidin (SAv) to CD SAM via orthogonal host–guest and SAv–biotin interactions [78]. The orthogonal linkers consist of a biotin functionality for binding to SAv and adamantyl functionalities for host–guest interactions at CD SAM. The approach was used for build up and patterning of protein nanostructures at interfaces using a sequence of host–guest and SAv–biotin interaction.

The encapsulation of anionic dyes in immobilized dendrimers has been described to occur via orthogonal multivalent host–guest and electrostatic interactions [79]. Fifth-generation poly(propylene imine) dendrimers, modified with 64 apolar adamantyl groups, have been immobilized on cyclodextrin host monolayers

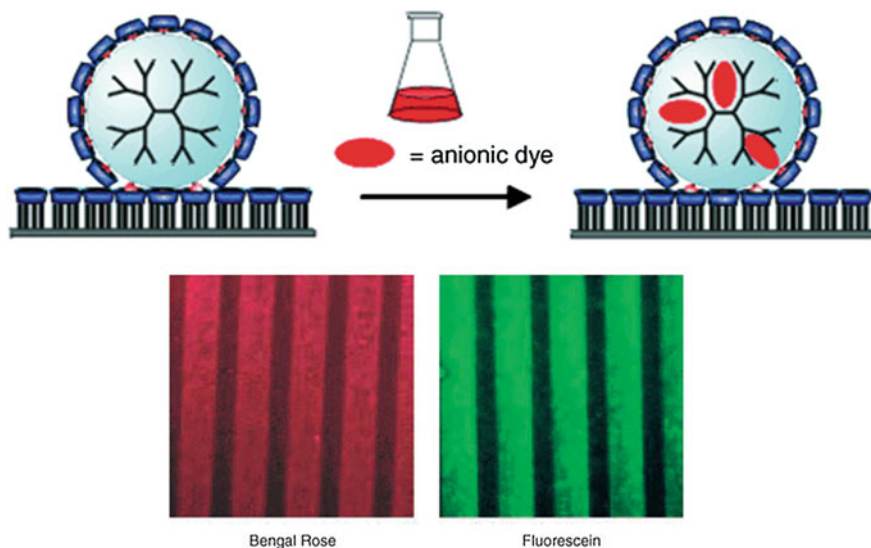


Fig. 2.18 Schematic representation of the filling of immobilized dendrimer patterns with anionic dyes (*upper*). Confocal microscopy images after microcontact printing of dendrimer on a molecular printboard, followed by filling of the immobilized dendrimers with Bengal Rose and fluorescein dyes (*lower*). Reproduced with permission from Ref. [79]. Copyright 2005 Wiley-VCH Verlag GmbH & Co. KGaA

on glass by supramolecular microcontact printing. The immobilized dendrimers retained their guest binding properties and functioned as “molecular boxes” that can be filled with fluorescent dye molecules from solution (Fig. 2.18).

The versatility and advantages of the molecular printboard for attaching proteins, for example, controllable binding constants and the suppression of non-specific interactions, were combined with His-tagged proteins via host–guest and metal–ligand interactions [80, 81]. His₆-tagged proteins have been attached to a molecular print board in a selective manner by using the supramolecular blocking agent **3** and Ni-**4** as depicted in Fig. 2.19.

Another contribution describes the patterning of silica substrates with thymine as hydrogen bonding unit and positively charged *N*-methylpyridinium-containing polymers using photolithography, and the subsequent orthogonal supramolecular modification of these surfaces using diaminopyridine-functionalized polystyrene and carboxylate-derivatized CdSe/ZnS core–shell nanoparticles through the combination of diaminopyridine–thymine hydrogen bonding and pyridinium–carboxylate electrostatic interactions (Fig. 2.20) [82].

The group of Haga developed DNA nanowires via orthogonal self-assembly by assistance of a SAM on the surface [83]. Orthogonal self-assembly was applied to the surface for the selective modification of the DNA capture molecules on the Au electrode. Two anchor groups of thiol and phosphonic acid were used to discriminate between Au and SiO₂, since a thiol group selectively attaches to the Au

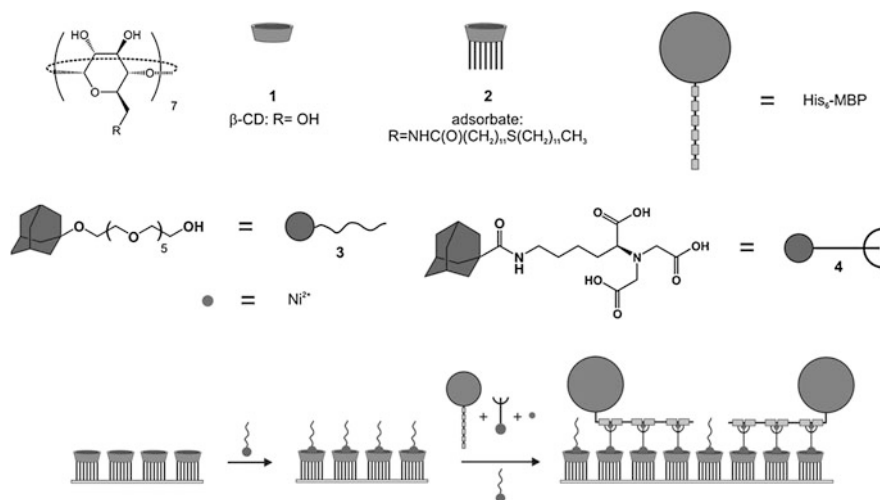


Fig. 2.19 Structures of compounds: β -cyclodextrin **1**, adsorbate for SAMs on gold **2**, adamantyl linkers **3** and **4**, nickel, His₆-MBP and cartoon for the binding of His₆-MBP through Ni-**4** to CD SAMs, in competition with monovalent blocking agent **3**. Reproduced with permission from Refs. [80, 81]. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA

surface and a phosphonate group attaches to the SiO_2 surface. Once the DNA trapping molecule is selectively attached to gold patterns on silicon substrate, DNA is captured from solution and used as a nanowire between two gold patterns (Fig. 2.21).

An example of the combination of electrostatic interaction with π - π stacking on a surface has been reported by Shinkai and coworkers [84]. They used a hexacationic homooxacalix[3]arene-[60]fullerene 2:1 complex to make a monolayer or a monolayer-like ultra-thin film on an anion-coated gold surface. They also studied the photoelectrochemical response of the monolayers under UV-irradiation (Fig. 2.22).

Tait et al. developed the concept of stabilizing and ordering 1D coordination structures at a surface [85]. Hydrogen bonding interactions with the second molecular species improved the stability and ordering of the copper-pyridyl 1D coordination chains. This combination of the selective orthogonal interactions allowed the fine-tuning of the supramolecular system by choice of the building blocks. In the group of Dalcane, hierarchical assembly on silicon using host-guest and hydrogen bonding interactions was developed [86]. The multistep growth of supramolecular structures on the surface resulted from the combined use of orthogonal host-guest and hydrogen bonding interactions. Using this strategy, hybrid and multifunctional materials could be constructed. Fasel et al. reported the two-dimensional mono- and bicomponent self-assembly of three closely related diaminotriazine-based molecular building blocks and a complementary perylene-tetracarboxylic diimide with the interplay of hydrogen bonding, dipolar interactions,

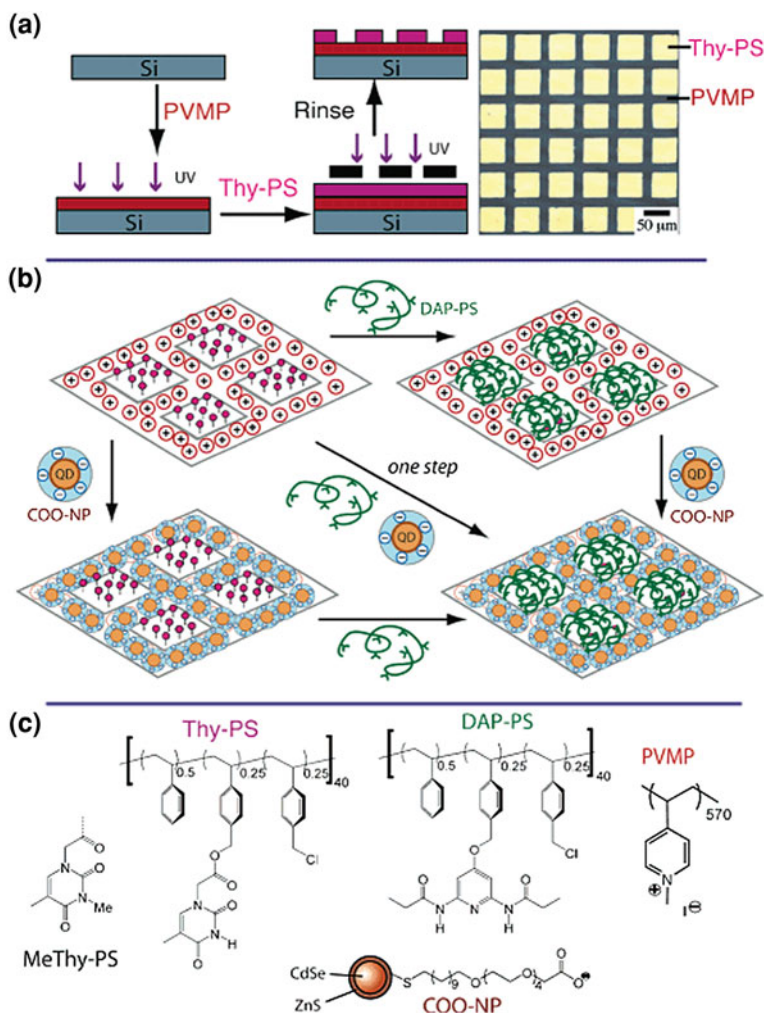


Fig. 2.20 Schematic illustration of the fabrication process. **a** Formation of the patterned PVMP/Thy-PS surface and optical micrograph of the resulting pattern. **b** One-step and sequential orthogonal functionalization by DAP-PS and COO-NP through PS-Thy:PS-DAP recognition and PVMP:COO-NP electrostatic interactions. **c** Chemical structures of the materials, including control polymer MeThy-PS. Reproduced with permission from Ref. [82]. Copyright 2006 American Chemical Society

and metal coordination [87]. They showed that the simplest molecular species, bis-diaminotriazine-benzene, only interacts via hydrogen bonds and forms a unique supramolecular pattern on a gold surface. For the two related molecular species, which exhibit in addition to hydrogen bonding also dipolar interactions and metal coordination, the number of distinct supramolecular structures increases

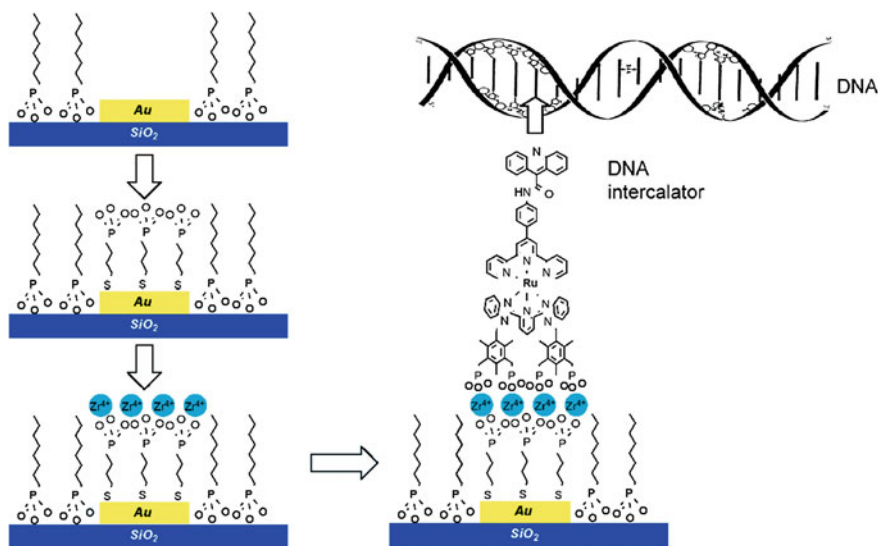


Fig. 2.21 Schematic illustration of surface modification for DNA capture by metal coordination-directed orthogonal assembly on gold-patterned silicon. Reproduced with permission from Ref. [83]. Copyright 2008 American Chemical Society

dramatically with the number of possible hierarchical assemblies with orthogonal interactions.

2.5 Conclusions

The use of supramolecular chemistry and molecular self-assembly including hydrogen bonding, metal coordination, electrostatic and host–guest interactions to direct the immobilization of functional systems on surfaces have attracted considerable attention in modern research due to their special characteristic features such as high specificity, controlled affinity, and reversibility. In this chapter some examples of orthogonal supramolecular interactions for the construction of functional materials with tunable properties on flat surfaces have been reviewed. Although these noncovalent interactions were used in many studies individually to build supramolecular architectures on surfaces, there are only limited numbers of examples that address the combination of different supramolecular interactions for the generation of functional monolayers. Hence, the development of hierarchical assemblies by using the combination of different noncovalent interactions still requires more efforts to allow the fabrication of functional surfaces. In this thesis, the concept of orthogonal supramolecular assembly is employed to form functional monolayers that are promising in sensor applications.

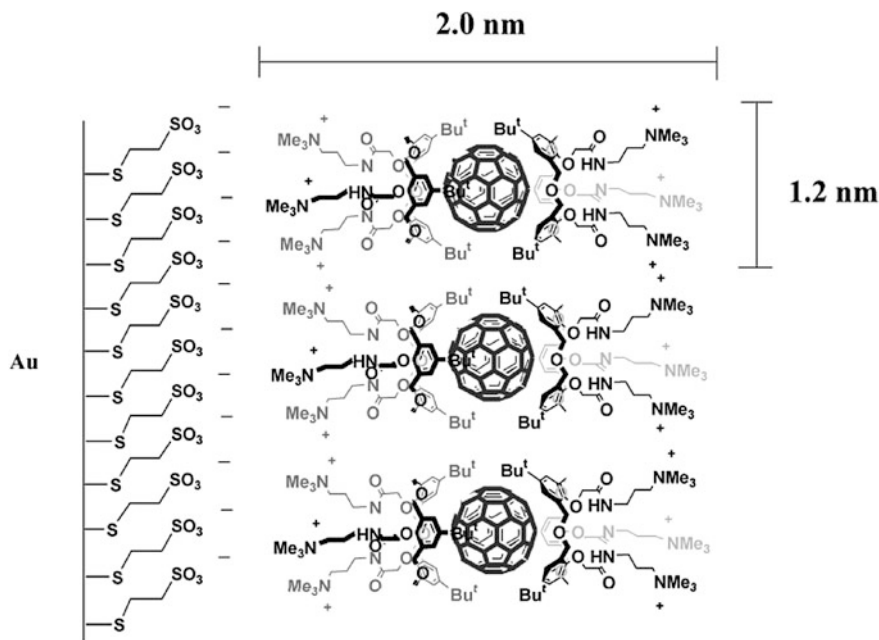


Fig. 2.22 Adsorption of sodium 2-mercaptoethanesulfonate (*first layer*) and 1-[60]fullerene (*second layer*) on a gold surface. Reproduced with permission from Ref. 84. Copyright 2000 The Royal Society of Chemistry

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Functional Monolayer Architectures

Yilmaz, M.D.

2012, XIX, 101 p. 69 illus., 51 illus. in color., Hardcover

ISBN: 978-3-642-30256-5