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Functional Reversible Switches Based on Imine-Derived Self-Assembled Monolayers on Gold

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“路漫漫其修远兮，吾将上下而求索。”—《离骚》（屈原著）

“The way was long, and wrapped in gloom did seem,
As I urged on to seek my vanished dream.”

— *Li Sao* (Author: Qu Yuan), is one of the greatest poems in Chinese poetry, translated by Xian-Yi Yang and Gladys Margaret Tayler (Nai-Die Dai).

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1. INTRODUCTION

1.1 Self-Assembled Monolayers (SAMs)

1.1.1 Concepts, Preparation, and Applications

A Self-assembled monolayers (SAM) are two-dimensional organized layers of organic molecules that spontaneously forms on appropriate substrates based on strong interactions between ligands and surface.[1-3] Initial work describing the self-assembly of surfactants on a metal surface to form a monolayer was performed by W. A. Zisman et al.[4] In the 1980s, SAMs received extensive attention. In groups of J. Sagiv[5,6] and A. Ulman,[7,8] different silane derivatives were coated on hydroxylated surfaces (silica, glass, etc.) to yield organic monolayers. During the same period, the adsorption of organic disulfides on gold surfaces was achieved by R. Nuzzo and D. Allara.[9] Afterwards, SAMs on different substrates were prepared and intensively studied by various characterization methods.

Generally, SAMs are produced by the absorption of suitable surfactants either from dilute solution or vapor phase. Liquid-phase deposition is a convenient and sufficient method, which can be accomplished in any ordinary laboratory. On the other hand, vapor phase deposition requires ultra-high vacuum equipment. It is often applied in some cases, where high level of a substrate purity is necessary or to provide opportunities for real-time surface characterizations.[10]

In principle, self-assembling surfactants consist of three parts, i.e. head groups, linker groups, and reactive terminal/end groups (Figure 1.1). Head groups are normally hydrophilic and possess favorable and specific affinities for surfaces. During the self-assembly process, they occupy all available binding sites on the surface as much as possible through chemical bonds or by other noncovalent interactions. Consequently, a monolayer with high chemical and thermal stabilities is formed and remains stable even after the rinse treatment.[1,10] Besides the two most popular SAM systems mentioned above, e.g. silanes on SiO_2 and disulfides or thiols on gold, other molecules with different head groups can be utilized for SAM production: phosphates and phosphonates for metal oxides,[11,12] fatty acids for aluminum oxide[13] and silver,[14] isonitriles for platinum,[15] and so on.

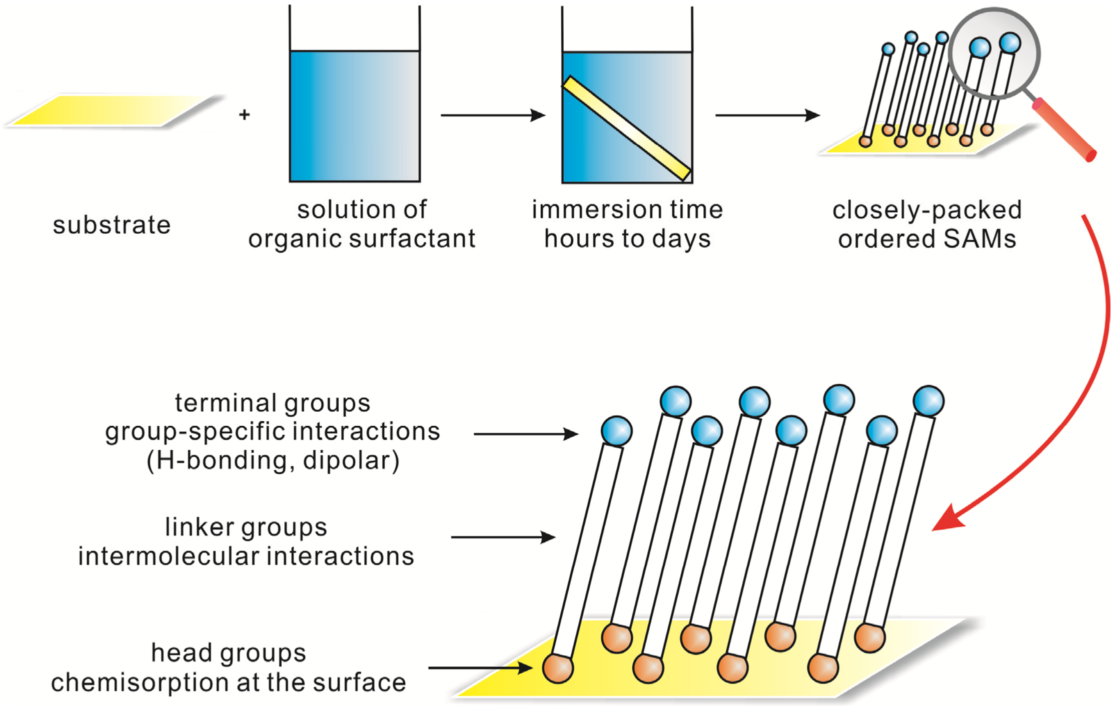


Figure 1.1. Preparation of SAMs by means of chemisorption. Driving forces for the spontaneous formation of this two-dimensional assembly include chemical bond formation or noncovalent interactions between head groups and surface as well as intermolecular interactions.[2] Adapted with permission from reference 2. Copyright © 1996, American Chemical Society.

The linker groups that have been studied most so far are alkyl groups. They play an important role in the construction of an ordered and closely packed SAM due to interchain van der Waals interactions to a order of few (<10) kcal/mol.[10] In the case of molecules incorporating a rigid π system, such as phenyl rings, π-interactions need to be considered. The strength of these intermolecular interactions determines the spacing between the head groups and thus affects the interface properties.[1]

The end groups can be either simple methyl groups or active groups. Simple and flexible modifications of active terminal groups by focused electron beam,[16] ultraviolet irradiation,[17] or chemical reaction[18] would render novel interfaces with specific chemical and physical characteristics like wetting,[19,20] corrosion resistance,[21] and biocompatibility.[22,23]

Nowadays, SAMs are very important for nanoscience and technology and are widely applied in materials, electrochemistry, biology, etc. because of their unique structure. For instance, densely packed stable SAMs can prevent substrates from corrosion and wear.[21] Moreover, their well-defined composition, structure, and potentially biocompatible terminal groups allow them to be used in chemical or biochemical sensors.[24,25] SAMs are a promising component in electro-optic devices based on their high molecular order parameter.[26] In addition, SAMs are advantageous in the nucleation of crystals in different configurations depending on tunable compositions and orientations of the terminal groups.[27,28]

1.1.2 Monolayers on Gold Substrates

Since gold has several unique advantages compared to other surface materials, it remains a standard substrate for SAM investigations despite its high cost.[3] Firstly, gold is readily available whether as a thin film or as a colloidal dispersion. In general, thin films of gold normally can be prepared by the physical vapor deposition (PVD) method,[29] whereas gold colloids are synthesized by chemical methods in solution, the details of which will be discussed in Section 1.3.1. Secondly, inertness is a peculiar characteristic of gold, which endows it with perfect stability in the presence of oxidants (at the temperature below its melting point) and most chemicals. Therefore, experiments of gold-based SAMs can be done under ambient conditions. An ultra-high vacuum (UHV) system is not necessary. On the other hand, strong chemical interactions between gold and sulfur derivatives result in easier formation of SAMs utilizing thiol chemistry. Third, as a non-toxic and biocompatible material, gold is suitable for biological studies.[30] Fourth, thin films of gold are common substrates used for multi-technology characterization, including infrared reflection absorption spectroscopy (IRRAS), surface plasmon resonance (SPR) spectroscopy, and ellipsometry. Lastly, easy cleaning procedures, well-defined surfaces, as well as capabilities for chemical etching[31] and photolithography[32] are additional advantages.

1.1.2.1 Preparation of Planar Gold Thin Film

Productions of planar gold thin films on substrates, e.g. glass, silicon, mica and plastic wafers, are commonly performed via physical vapor deposition (PVD) method, including thermal vapor deposition, electron beam vapor deposition, and sputtering.[29] In the case of gold supported glass and silicon wafers, adhesion layers made of titanium, chromium, or nickel with thickness of 15-50 Å have to be deposited first onto the substrates in order to improve the adhesion of the gold film, especially when substrate has an oxidized surface. Since some of these adhesion layers could diffuse into the gold upper layer over time and contaminate it,[33] titanium is the only viable choice when organisms (e.g. cells) are studied on the gold surface owing to its non-toxicity. By this means, polycrystalline gold thin films composed of contiguous islands or grains, having a dominant (111) surface, deposit in a thickness ranging from 100 to 1000 Å.[34] To obtain higher adhesion, less surface roughness, and higher reproducibility, substrates must be cleaned oxidatively (i.e., by oxygen plasma) prior to the coating. Besides of the substrate purity, level of vacuum, and other experimental conditions, these methods lead to gold thin films of greatly varying purity and grain morphology. For example, when the temperature of the substrates is increased from room temperature to 400 °C in the thermal vapor deposition process, the size of gold grains becomes larger and the shape simultaneously changes from round to terraced.[35] Furthermore, incidence angles of deposited gold on substrates[36] and compositions of thin films also influence the average size of grains, which determine these substrates are useful for the different applications. On the other hand, even if the preparation of gold thin film has been done, the topography of these films still can be changed by thermal annealing[37] or chemical treatment with strong acid.[3]

Deposition of gold on freshly cleaved mica substrates provides thin films with well-defined and large terraces, which are especially suitable for atomic force microscopy (AFM) and scanning tunneling microscopy (STM) measurements of ultra-thin monolayers.[38]

1.1.2.2 Head Groups for Gold: Thiols, Disulfides, and Sulfides

The first example of the fabrication of SAMs of dialkanedisulfide (RS-SR) on a gold surface was reported by R. Nuzzo and D. Allara in 1983.[9] Subsequently, substantially different organic compounds have been synthesized, unveiling a relationship between head groups and formations of ordered monolayers. For example, Bain et al. [39] systematically studied the adsorption of molecules possessing different head groups, e.g. amino ($-NH_2$), hydroxyl (-OH), carboxyl (-COOH), cyano (-CN), phosphine (PR_3), sulfide (-S-), disulfide (-S-S-), and thiol (-SH), onto gold. All corresponding SAMs were characterized by contact angle measurement and ellipsometry to evaluate surface hydrophilicity and layer thickness. The results demonstrated that only phosphorus and sulfur molecules spontaneously assembled on the surface to form closed-packed and ordered monolayers, which is attributed to strong interactions of gold with phosphorus and sulfur. A following competition experiment[39] indicated that thiol had an even higher affinity to gold than phosphine.

In the light of its high affinity to gold and good solubility in organic solvents, thiols are currently the most used ligands for SAM formation. Alternatively, disulfides were corroborated to produce a similar monolayer structure as thiols if the conditions of the sample preparation have been carefully controlled.[40,41] However, a multilayer formation has been observed in this case.[42] Compared with the oriented and ordered SAMs produced by thiols or disulfides, SAMs from sulfides are less stable and less ordered,[43] although their oxidation resistance makes sulfides more easily handled during experiments.

Three different mechanisms for the spontaneous assembly of SAMs from thiols, disulfides, and sulfides on gold surface, by formation of gold-thiolate bonds or dative bonds, have been proposed based on previous comparative studies. In the case of alkanethiols, although the mechanism involved in the reaction has not been completely understood, a two-step mechanism, oxidative addition of the S-H bond to the gold surface followed by a reductive elimination of hydrogen, was suggested.[2,44,45] If the SAM formation is performed in the complete absence of oxygen, the process can be illustrated as follows:

$$\text{R-S-H} + \text{Au}_n^0 \rightarrow \text{RS}^-\text{Au}^+ \cdot \text{Au}_n^0 + 1/2\ \text{H}_2$$

Otherwise, the released H associates with oxidants and converts to water:

$$\text{R-S-H} + \text{Au}_n^0 + \text{oxidant} \rightarrow \text{RS}^-\text{Au}^+ \cdot \text{Au}_n^0 + 1/2\ \text{H}_2\text{O}$$

However, because the detection of hydrogen during self-assembly is difficult, controversy over this mechanism has existed for a long time. For example, Nuzzo et al.[46] and Rzeźnicka et al.[47] both reported nondissociative chemisorptions of short-chain alkanethiols on Au(111). In 2009 when Kankate et al.[48] investigated vapor-deposited aromatic SAMs by means of *in situ* X-ray photoelectron spectroscopy, however, experimental data clearly indicated a partial reduction of monolayer-terminal nitro groups to amino groups, which is evidence for the hydrogen generated upon the thiol adsorption. Moreover, another theoretical study about the formation of alkanethiol SAMs on Au(111) concluded that the mechanism of S-H bond breakage was reasonable.[49]

The chemisorption of dialkyldisulfides onto gold yields SAMs by a similar means as thiols, where gold thiolate species form after a simple oxidative addition of the S-S bond to gold, which was proven by Biebuyck et al.[50] twenty years ago.

$$\text{RS-SR} + \text{Au}_n^0 \rightarrow \text{RS}^-\text{Au}^+ \cdot \text{Au}_n^0$$

In the same study, an additional thiol molecule was chosen to perform a replacement experiment on pre-prepared SAMs from asymmetrical disulfides containing approximately equal proportions of the two thiolate groups. XPS data showed that one thiolate group was replaced about 10^3 times more rapidly than another thiolate group, which suggests that these two thiolates formed from a single disulfide behave as independent entities in their subsequent reactions.[50]

In the above two cases, an exothermic covalent gold-thiolate bond formation is one of the most important driving forces for self-assembly. Thermodynamic analysis[51,52] demonstrated the strength of this bond to be about 45-50 kcal/mol, thus leading to robust and stable conformations of SAMs.

Unlike thiols and disulfides, sulfides assembled on gold in a different manner: via a nondissociative (S-C bond) adsorption process,[53] followed by the formation of a dative bond between sulfur and gold rather than gold-thiolate.[54] Therefore, this kind of monolayer is less stable and with less maximum coverage as a result of the relatively weaker S-Au interaction. Furthermore, numerous contaminants remain on the substrate, in contrast to the cleaner case of thiols/disulfides.[55,56]

1.1.2.3 General Protocol and Experimental Factors

Generally, SAMs on gold surfaces can be prepared via the spontaneous adsorption of organosulfur precursors (thiols, disulfides, sulfides, etc.) from either a liquid or a vapor phase. The widely-used protocol for the case of the liquid phase is to immerse a freshly prepared and cleaned gold slide into a dilute organic ethanolic solution (e.g. ~1-10 mM) for ~12-18 h at room temperature. Afterwards, the resulting monolayer is rinsed with ethanol and dried under a clean inert gas stream.[3]

As a result of the poor solubilities of some organosulfur molecules in ethanol, especially disulfides, tetrahydrofuran (THF) and acetonitrile can be used as alternatives. No abnormal contact angle values are observed because, like ethanol, these two solvents do not incorporate into the monolayer.[57] The direct fabrication of carboxylic acid-based SAMs on gold surface can result in the formation of bilayer due to intermolecular hydrogen bonding (Figure 1.2). Nevertheless, an optimized choice of solvent can solve this problem and lower the level of surface roughness.[58]

The alkyl chain length is another factor for the construction of SAMs. With the increasing number of methylene units in alkanethiols, intermolecular van der Waals interaction becomes stronger, which promotes the spontaneous assembly and thereby affects the structure of monolayers.[57] In addition, an odd-even effect of alkane chain carbon number was reported by W. Azzam,[59] where oligo-*para*-phenyl-substituted alkanethiols with an odd number of methylene units achieved a higher packing density and a smaller inclination of the phenyl groups compared to thiols with an even number of methylene units. In other words, the orientation of the phenyl backbone in the former case was almost perpendicular to the surface. This could be interpreted by the binding modes of sulfur on gold (Figure 1.3), in which surface-S-C angle is about 104 °, close to what is expected from sp^3 hybridization geometry.[60,61]

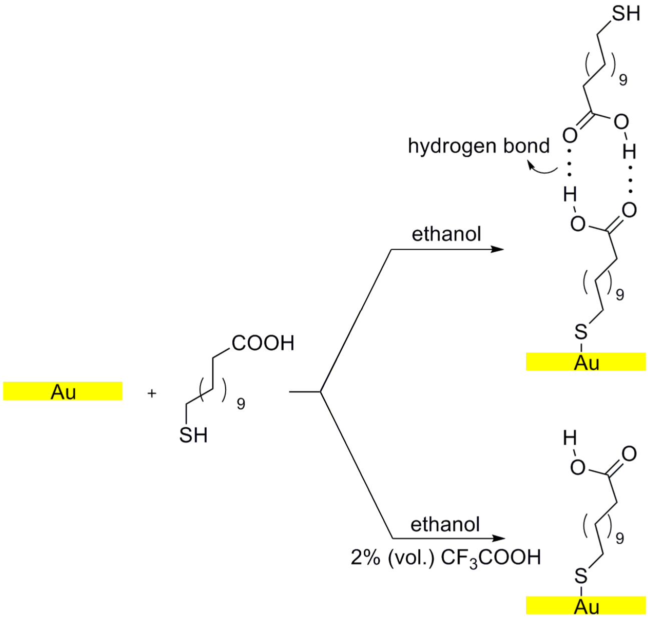


Figure 1.2. Schemes of the structures of -COOH terminated SAMs prepared in ethanol and in the optimized solvents.[58] Adapted with permission from reference 58. Copyright © 2005, American Chemical Society.

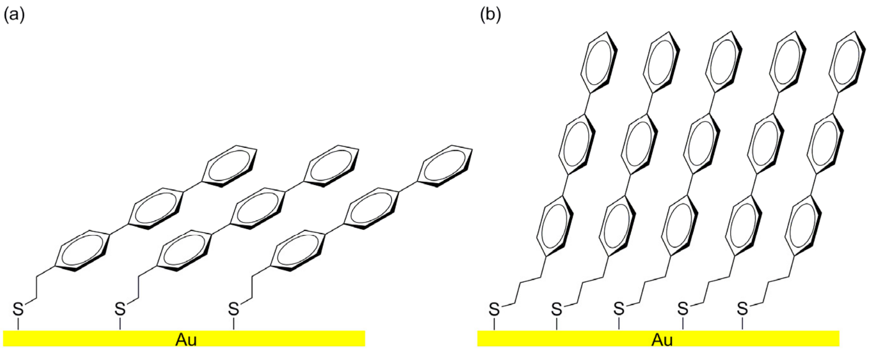


Figure 1.3. Structural comparison of SAMs coated by oligo-*para*-phenyl-substituted

alkanethiols with an even number of methylene units (a) and an odd number of methylene units (b).[59] Adapted with permission from reference 59. Copyright © 2006, American Chemical Society.

The self-assembly of organic molecules from liquid phase on substrates is a very complex process. Besides these two factors of solvent and chain length, the configuration of adsorbates,[62,63] temperature,[59] and the concentration of oxygen in solution[64] have considerable bearing upon the monolayer formation, and kinetics, stability, structure, and morphology of the responding SAMs.

SAMs deposited from the gas phase generally presented similar results as those obtained from liquid phase under normal conditions.[46,48] This method is usually applied for in-situ characterization and to prepare an ordered monolayer with a "lying-down" phase. A disadvantage is that some volatile low molecular weight compounds cannot be used as precursors.

1.1.2.4 Growth Mechanisms of SAMs

To understand this self-assembly process, Bain et al.[57] carried out kinetic studies of alkanethiols on Au(111). The results of contact angle and ellipsometry measurements demonstrated that, 80-90% of final values were already reached within the first few minutes. The self-assembly process was only completely achieved after several hours, however, and the final film properties were constant. Additionally, STM microscopy performed by Sun et al.[65] supported the claim that monolayer defects disappeared after a long immersion time of several hours. Therefore, it is likely that the self-assembly is not a simple one-step process. Moreover, Poirier et al.[66] and Schreiber et al.[67] discovered the growth mechanism of alkanethiols on gold from the vapor phase via in-situ multi-technique characterizations. They found that some molecules first adsorbed on the surface with flat lying configurations to form islands of "striped" phases. Afterwards, with continued deposition, these islands further grew and finally "stood up" to give an orientation nearly perpendicular to the surface. If experiments were performed above 15° C, a two-dimensional liquid-like intermediate phase was also observed between the "striped" phase and the final solid phase.[67]

All of this experimental evidence indicated that monolayer growth was a stepwise process consisting of transport, adsorption onto the interface governed by interactions between gold and head groups, and subsequent two-dimensional self-organization, in which chain-chain interactions and flexibilities of the chains on the surface play important roles.[2,68] Firstly, surfactants are transported onto the interface via diffusion and convection. Initially, molecules are randomly adsorbed on the surface with a disordered conformation forming the first low density state. Undergoing a long period of self-organization, a high density "solid" phase eventually emerges, where all molecules ordered are arranged and closely packed.[68]

In a review,[68] Schwartz summarized the general growth mechanism by a cartoon sketch (Figure 1.4). In this scheme, three different intermediate phases, i.e., a coexistence region where islands of solid phase are surrounded by isolated adsorbate molecules, a disordered two dimensional liquid phase, and an ordered phase with lower density, such as the "striped" phase, are depicted.

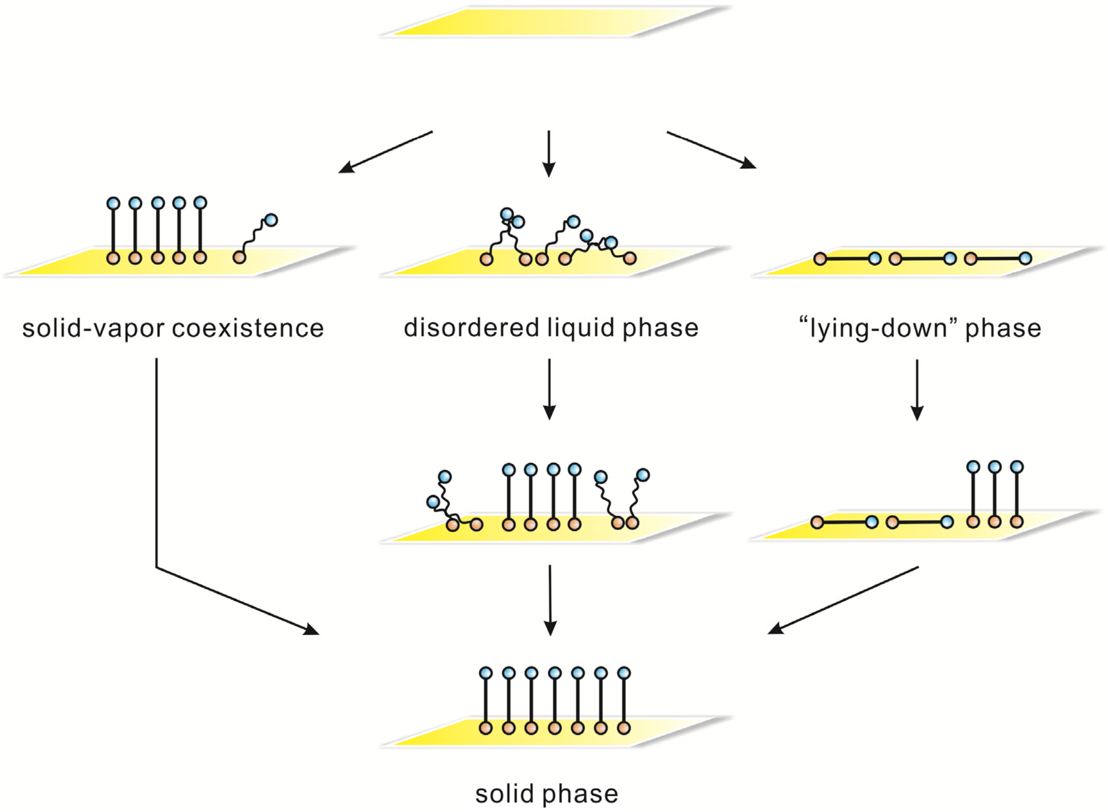


Figure 1.4. Illustration for describing the self-assembly process of surfactants on the surface through three different intermediate phases.[68]

1.1.2.5 Mixed-SAMs

A mixed-SAM is a monolayer composed of two or more different molecules and provides a methodology to diversify interface properties. Thereby, it could have promising application in the development of biosensors and cell biology.[69,70] Currently, mixed-SAMs can be synthesized by several methods as following: First, by dissociative adsorption of asymmetric disulfide (Figure 1.5a)[71,72] and second, by coadsorption from a solution containing two different thiols (Figure 1.5b).[39,73,74] However, the concentration ratio of the two components in the produced mixed SAMs was found to deviate from that in the solution.[39] Clear island formation was observed as well in some cases, where for example the concentration ratio of C_4H_9SH to $C_{18}H_{37}SH$ in the solution are 20:1 or 40:1 reported by Tamada et al.[75] An attempt at combining these two methods for mixed asymmetric disulfides (Figure 1.5c) formed more homogeneous SAMs compared with the mixed thiols.[76] Third, there is a partial ligand exchange on the prepared chips (Figure 1.5d).[77] Moreover, chemical modification[78] and adsorption of asymmetric dialkylsulfides are also effective and convenient means.

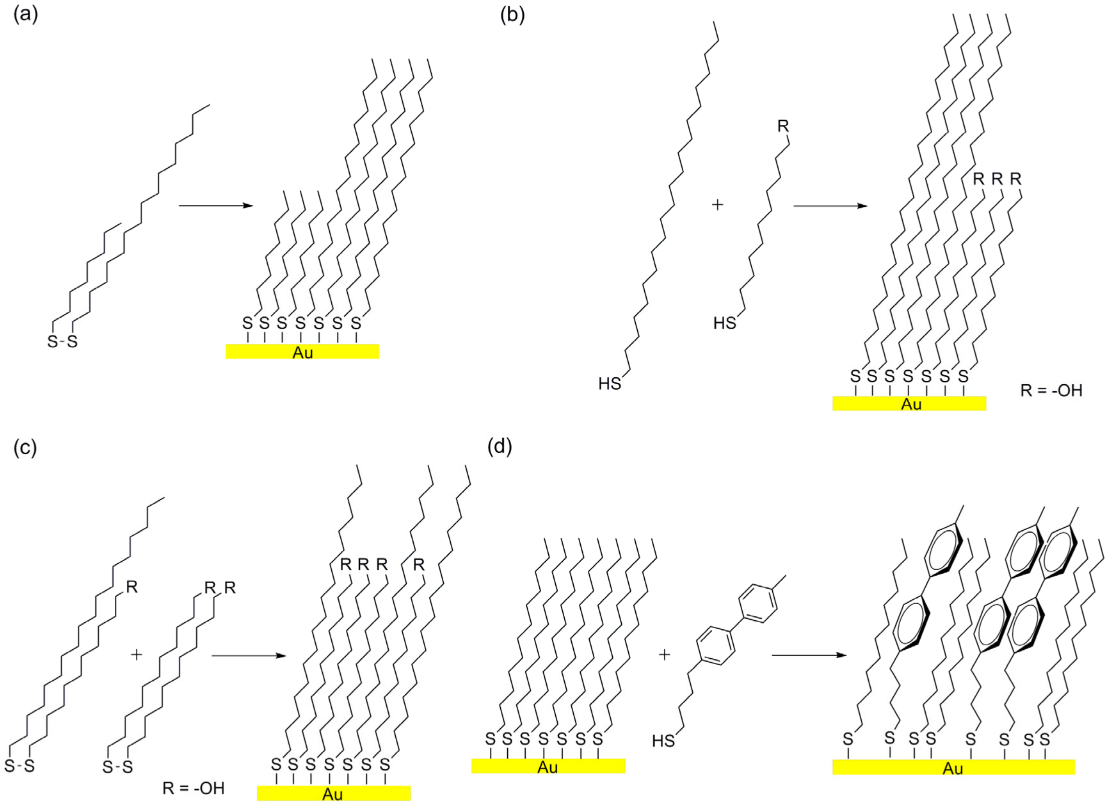


Figure 1.5. Illustration of mixed-SAMs synthesized by asymmetric disulfide (a),[71] coadsorption of thiols (b),[73] adapted with permission from reference 73, copyright © 1989, American Chemical Society, coadsorption of mixed asymmetric disulfides (c),[76] adapted with permission from reference 76, copyright © 2001, American Chemical Society, and ligand exchange (d),[77] respectively.

1.1.3 Multi-technique Characterization of SAMs

Once SAMs have been constructed, surface and bulk properties need to be studied via different analytical tools. Ellipsometry is a common optical technique for determining thickness ranging from nanometer to several micrometers and the uniformity of freshly prepared monolayers.[1,79] The wettability of a surface is generally evaluated by its contact angle with different liquids, in other words, where the liquid/vapor and solid/liquid phases meet, and by the resultant interaction between the interfaces.[80] The wettability is determined to be superhydrophilic, hydrophilic, hydrophobic, or superhydrophobic according to the size of the contact angle θ with a suitable liquid, e.g. water (Figure 1.6). Besides the static sessile drop method, dynamic sessile drop method for measuring advancing and receding contact angle is used as well. Contact angle measurements not only indicate the surface wettability, but also give information about the surface composition and the structure, especially for the study of mixed SAMs.[81,82]

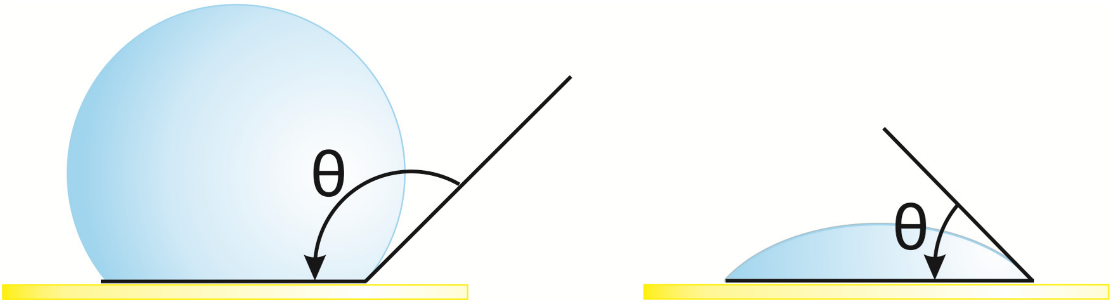


Figure 1.6. Contact angle of water on hydrophobic (left) and hydrophilic (right) surfaces.[1]

Fourier transform infrared (FTIR) spectroscopy is a powerful tool for investigating the molecular packing and orientation in the thin film.[1] Two main modes, attenuated total reflection (ATR) and grazing-angle (GA), are commonly used to characterize surfaces. In the case of grazing-angle FTIR spectroscopy, for example, a high angle of incidence, e.g. 80-85°, is applied in order to efficiently measure the reflection-absorption spectrum.[83] By this method, the direction of the transition dipoles of molecules and then the orientation of the molecules on the surface can be extrapolated on the basis of the surface dipole selection rule, which points out that only vibrational modes with a transition dipole or a component of the transition dipole perpendicular to the surface can be observed in infrared spectroscopy on metal surfaces.[84]

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique for analyzing surface compositions and elemental chemical states in the range of nm scale in a film.[1] Although XPS gives a relatively low spatial resolution, it still is a fruitful tool for characterizing single component SAMs and mixed SAMs. For obtaining images of SAMs with an atomic resolution, scanning tunneling microscopy (STM)[85] and atomic force microscopy (AFM)[86] have been utilized. So far, these methods are extensively applied in in-situ kinetic studies for SAM growth and for measuring and manipulating single molecules on surfaces.

1.2 Reversible Photo-induced Isomerization in Solutions

1.2.1 Background and Survey History

Reversible photo-induced isomerization is one kind of reaction upon exposure to light, resulting in a reversible transformation of a molecule between two different isomeric states.[87] In this reaction, some molecules normally undergo color changes after photoirradiation, and therefore are called photochromic compounds. Photochromism is defined for this phenomena, or is more accurately described as a reversible transformation of a chemical species by absorption of electromagnetic radiation between two forms with different absorption spectra.[88,89] The first report on photochromism was given by Fritsche[90] in 1867, in which reversible color changes of tetracene between orange and colorless under conditions of light and heating were introduced. In the following half century, the studies of photochromism focused more on different compounds, [87] including benzalphenylhydrazone[91] and osazone.[92] From 1940 onward, the interests in photochromism moved to investigations of a mechanism of the photochromic process and structures of intermediates and products. Afterwards, with a development of physical techniques such as the discovery of flash spectroscopy, the understanding of the reactivities of photochromic molecules and their corresponding excited states became possible. So far, many of the photochromic compounds have been found and synthesized (Table 1). More attention has been devoted to the reversible conversions of properties (e.g., optical, chemical, electrical, and bulk) in these compounds and materials.[87] In the next sections, some of these photochromic compounds will be introduced and compared.

1.2.2 *cis-/trans-* (*Z*/*E*) Isomerization

1.2.2.1 Azobenzene

E/*Z* isomerization is a type of stereoisomerization involving the orientations of functional groups in a molecule containing double bonds, e.g., -N=N-, -C=C-, -C=N-, etc. An aromatic molecule possessing a diazene group –N=N- in conjugation with two phenyl substituents is commonly called an azobenzene, which is interesting due to its transformation between *E* and *Z* configurations upon external stimuli (Table 1, entry 1). The first reversible *E*/*Z* isomerization of azobenzene was observed by Hartley in 1937 during a determination of its solubility.[93] He not only observed the color change of azobenzene solution exposed to sunlight that was made reversible by keeping the solution in the dark but also isolated a product from this photochemical reaction. Eventually, the isolated compound was identified as the previously unknown *Z*-azobenzene isomer after chemical and physical characterizations. In order to acquire higher quantum yield in the process of *E* to *Z* isomerization, radiation with an appropriate wavelength, at which the *trans*-isomer has a higher absorption intensity than the corresponding *cis*-isomer, has to be chosen.[94] Thereby, analyses and understanding of electronic structures for azobenzene and its derivatives under different external conditions are essential.

A UV/Vis absorption spectrum of *trans*-azobenzene shows three absorption bands resulting from the electronic structure of the diazene group –N=N-: the lowest energy transition ($n \rightarrow \pi^*$, $\varepsilon \sim 500$) at 440 nm, the second transition ($\pi \rightarrow \pi^*$, $\varepsilon \sim 17000$) at 314 nm, and the highest energy transition localized in the phenyl rings ($\sigma \rightarrow \sigma^*$) at ca. 280 nm.[95] Certainly, these bands could undergo a certain degree of hypsochromic or bathochromic shifts owing to substitutent and solvent effects, among others. Depending on their reactivity, Rau[96,97] classified three types of azobenzene derivatives: azobenzene, aminoazobenzene, and pseudostilbene. Obviously, the azobenzene type of compounds affords similar spectra as the parent azobenzene. The main feature of the spectrum in this case is a large separation of the long wavelength band from the shorter wavelength bands. Moreover, substituents except for the amino group or solvents, only give a minor effect on the absorption spectroscopy for this class of compounds.[98] While in the aminoazobenzene-type system, molecules are functionalized with an electron donor group, such as $-NH_2$ or -OH on the *para*-position of azo ring. The $\pi\rightarrow\pi^*$ transition is lowered in energy and red shifted to the visible region, causing the two bands of $\pi\rightarrow\pi^*$ transition and $n\rightarrow\pi^*$ transition to overlap. Especially in an environment of polar solvent, such as ethanol, these two transitions may appear as one band.[98] If further substitution of an electron withdrawing group (-NO_2) on the opposite or 4'-position is carried out on an aminoazobenzene-type compound, such as 4-aminoazobenze, the band of $n\rightarrow\pi^*$ transition buries in the $\pi\rightarrow\pi^*$ absorption due to the still decreased $\pi\rightarrow\pi^*$ transition energy. Similarly, polar solvents furthermore enhance the red shift of $\pi\rightarrow\pi^*$ bands in this push-pull system.[99]

Since the energy of $\sigma\rightarrow\sigma^*$ transition is too high, the corresponding singlet state normally is not involved in the photo-induced *E* to *Z* isomerization, and thus no change of $\sigma\rightarrow\sigma^*$ absorption of azobenzene could be observed. On the other hand, both $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ bands shift to lower wavelength regions of 430 nm and 280 nm after the photo irradiation, respectively. Additionally, the transition of molecular configuration from a planar to a more three-dimensional one causes significant alterations of absorption intensities.[95] Compared to the *trans*-isomer, *cis*-azobenzene is thermodynamically unstable by about 56 kJ/mol.[100] The moderate activation energy (ca. 85-100 kJ/mol) allows *Z* to *E* isomerization of azobenzene derivatives to be accomplished by means of visible light or heat[101] although it is sometimes a slow process and takes more than a couple of hours at room temperature, e.g. the half-lifetime of this process at 25°C in the case of 4-dimethylaminoazobenzene was calculated to be 220 minutes.[102]

The change in molecular configuration of azobenzene attributed to the reversible *E*/*Z* photo-induced isomerization has been proven to have potential application in optoelectronics, biological science, and material technology.[97,103,104] For example, "molecular scissors" for light-triggered ion extraction and transport,[105,106] photo-responsive biomaterial to control protein activities in cell,[107] and light activated ion channel are recent systems that utilize the isomerization of azobenzene.[108] However, the stabilities of these systems still need to be further studied before they can be practically applied.

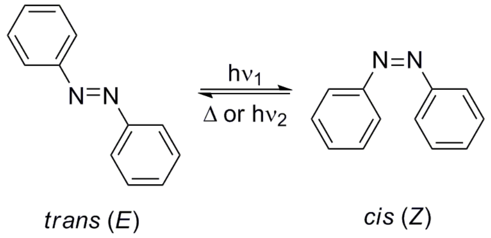
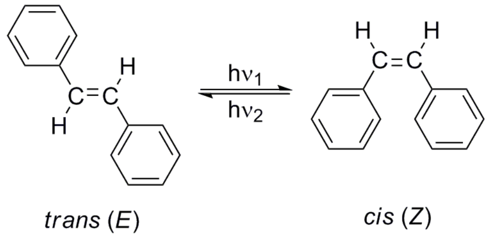
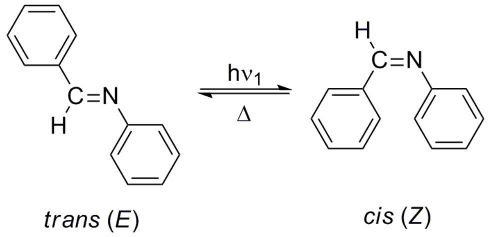
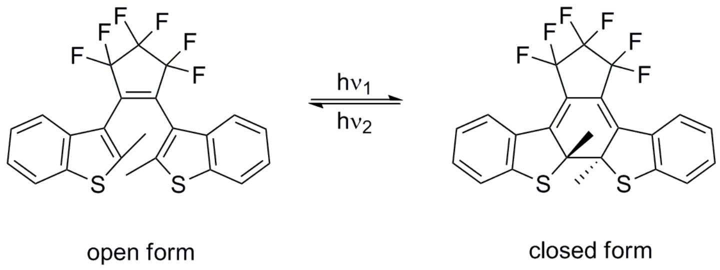
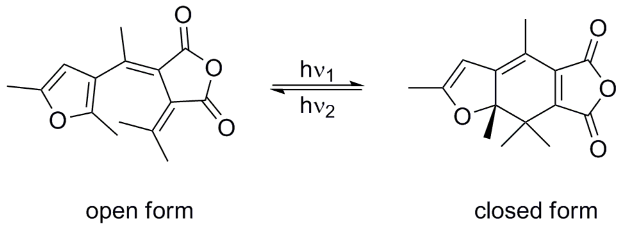
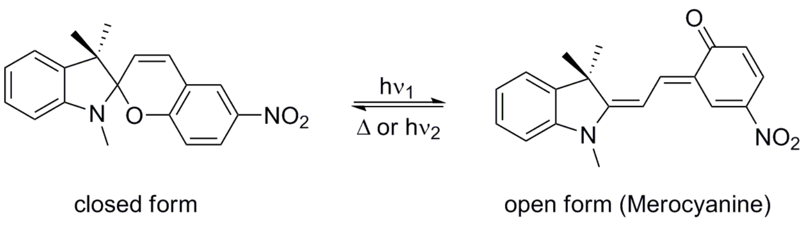
Entry	Compounds	Schemes
1	azobenzene	
2	stilbene	
3	imine	
4	diarylethene	
5	fulgide	
6	spiropyran	

Table 1: Some organic photochromic compounds for photo-induced isomerization.[87]

1.2.2.2 Stilbene

Similarly, stilbene, containing a C=C double bond, undergoes reversible *Z*/*E* isomerization as well (Table 1, entry 2). This process and the corresponding solvent substituent effects have been extensively studied since the middle of the last century.[109,110] It was found that *trans*-stilbene converted to the *cis*-isomer with a quantum efficiency of about 0.9 upon direct irradiation with light of 313 nm wavelength.[111] Light with a shorter wavelength could lead to lower conversion efficiency, however.[112,113] In contrast to *cis*-azobenzene, *cis*-stilbene is much more thermally stable as a result of smaller energy difference (10-20 kJ/mol[114], 56 kJ/mol in the case of azobenzene[100]) between the two isomers of stilbene. Furthermore, owing to a far higher energy barrier (ca. 170 kJ/mol)[115] in the thermal relaxation, *cis*-stilbene cannot be readily isomerized to the *trans*-isomer by simple heating. Experimental results demonstrated that only 8% conversion was observed after 20 h even at 214 ºC.[116] However, modifications of stilbene or introduction of catalysts could strongly influence activation energy and effectively promote the *Z* to *E* isomerization.[117,118]

Additionally, unlike azobenzene, there are several reactions competing with reversible *Z*/*E* isomerization in the case of stilbene (Figure 1.7).[119] One is the photodimerization of *trans*-stilbene that was first discovered by Ciamician and Silber in 1902.[120] This side reaction probably decreases the quantum yield of the isomerization from *E* to *Z*. Another is the electrocyclic rearrangement of *cis*-stilbenen.[112,121] In most systems, the produced dihydrophenanthrene (DHP) with a close-ring form could thermally relax back to *cis*-state in the absence of oxygen. Otherwise, oxidation of this form results in the formation of phenanthrene so that more and more *cis*-isomers are consumed and reversible photo-induced *E*/*Z* isomerization is hampered. Therefore, the applications of stilbene derivatives as light-driven molecular switches are sometimes limited.

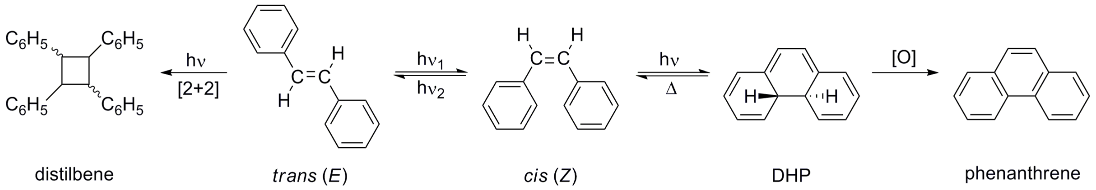


Figure 1.7. Two side reactions in the process of *Z*/*E* photoisomerization of stilbene: photodimerization and electrocyclic rearrangement.

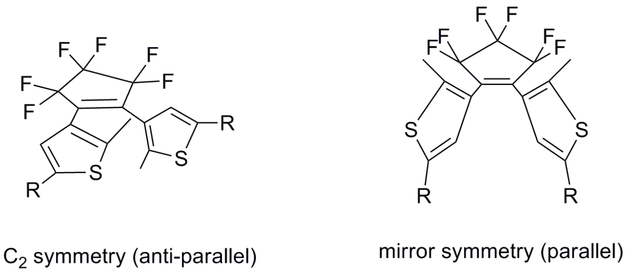
1.2.2.3 Imine

Imine, one type of chemical compound containing a C=N double bond, is photoisomerizable as well (Table 1, entry 3).[122] In contrast to azobenzene and stilbene, relatively little is known about the phtoisomerization of this compound due to the limited hydrolytic stability of this double bond. Imine derivatives can be readily synthesized via a coupling reaction of aldehyde (R-CHO) or ketone (R_1R_2CO) with an amine ($R'-NH_2$). Further functionalization on the two precursors easily provides diverse products. Therefore, the convenient chemical synthesis of imine derivatives is regarded as one of the advantages of this system. Furthermore, compared with azobenzene, only about half of the energy barrier needs to be overcome for managing the photo-induced *E* to *Z* transition. The activation energy of 16-17 kcal/mol in the thermal relaxation process[123] is also appreciably lower than for stilbene (42 kcal/mol)[124] and azobenzene (23 kcal/mol),[125] which leads to a far shorter half-life (about 1 sec. at 25° C) of the *cis*-isomer.[126] As a result, imine compounds could have potential application as a light-driven molecular motor, for which the extremely rapid reversible geometrical change under light stimuli is a prerequisite.[127]

1.2.3 Pericyclic Ring-Opening and Closure

In addition to the above-mentioned *Z*/*E* isomerization, reversible photo-induced isomerization can be accomplished in ring opening and closure systems as well by the electrocyclic mechanism. So far, these systems have gradually become promising candidates for chiroptical molecular switches. The transition process can be readily detected by means of circular dichroism (CD) and optical rotatory dispersion (ORD) attributed to differences in chirality between two states of the photochromic molecule.[128] The typical members of these systems, diarylethenes,[129] fulgides,[130-132] and spiropyrans[133,134] are recently being intensively investigated in regard to modification, photoswitching, and the corresponding applications.

The photoreactivity of diarylethenes (Table 1, entry 4) containing heterocyclic aryl groups is greatly affected by the molecular conformation, since in the two conformers of C_2 symmetry (anti-parallel) and mirror symmetry (parallel) (Figure 1.8) only the former has a capability to proceed by the conrotatory electrocyclic photocyclization reaction.[129] Therefore, in order to enhance the photoreactivity and the quantum yield of the cyclization, the ratio of anti-parallel conformers needs to be increased as much as possible via various methods, for example by the introduction of bulky groups at the 2 and 2'-positions of the benzothiophene rings,[135] or by embedding diarylethene derivatives into cyclodextrin cavities.[136] Due to their potential applications in fatigue resistance and their thermal stability, diarylethenes are indispensable compounds for exploitation in optoelectronic devices.[129]



C_2 symmetry (anti-parallel)

mirror symmetry (parallel)

Figure 1.8. Two different molecular conformations of diarylethene: anti-parallel (left) and parallel (right).[129]

Another system, the fulgides (Table 1, entry 5), has also shown a potential application as photo-mode rewritable recording media, although in the initial stage of the studies it was found that fulgide underwent some reversible and irreversible side reactions, e.g., hydrogen rearrangement and oxidation.[132,137,138] These drawbacks were eventually solved by Heller et al. by employment of heteroaromatic rings instead of the phenyl group[139] and by replacing all H atoms on ring closing carbon atoms by methyl groups.[140] Since then, thermally irreversible photochromic fulgides have been successfully prepared, which has permitted the investigation of their applications in optical devices.

Spiropyrans (Table 1, entry 6) were first proposed as a photochemical memory model by Hirshberg in 1955 when he observed reversible color changes of these compounds upon photo irradiation, which resulted from an interconversion of the closed spiropyran state and the open merocyanine state.[141] Afterwards, substantial research to discover the reversible physical and chemical properties of spiropyran-like compounds under similar conditions was carried out. The corresponding results and applications as photochromic materials, optical recording media have been reviewed.[128,132,134]

1.3 Reversible Photo-induced Isomerization on Surfaces

Ways to take advantage of the unique properties of photo-responsive molecules to achieve their photo-induced isomerization on surfaces is a challenging topic of intense research. Among these molecules, azobenzene derivatives are most studied due to their higher quantum yields of the photoisomerization in solution, simple molecular structures, and relatively good stability of both isomers. In the next sections, research about the photoisomerization of azobenzene molecules in SAMs on gold nanoparticles and gold planar surfaces will be introduced.

1.3.1 Gold Nanoparticles

Since ancient times, gold colloids have been used in decoration and even in medicine, although their exact nature was unknown at that time. The initial scientific research about gold nanoparticles (Au NPs) was carried out by Faraday. In 1857, he published the first paper of Au NPs and articulated that a red color of the Au NPs solution is related to their colloid nature.[142] Consequently, researchers observed the size-dependent surface plasmon absorption band of Au NPs when their size is above 3 nm. Nowadays, gold nanoparticles are widely applied in areas of biology, biomedicine, catalysis, and electronics owing to their special nanoscale sizes and their peculiar optic properties.[143-145]

The synthesis of gold nanoparticles can be accomplished either in aqueous solution or in organic solvents, where the produced nanoparticles have diameters ranging from one to hundreds of nanometers. In the typical procedure, gold(III) salts (e.g. $HAuCl_4$) are first reduced to Au^0 by different reducing agents. Surfactants are subsequently added to stabilize the gold colloids via strong Au-S chemical bonds or other kinds of ligand-substrate interactions to form gold nanoparticles of reduced polydispersity and controlled size (Figure 1.9).[146] The two most popular methods are citrate reduction[147-149] and the Brust-Schiffrin method.[44,150] The citrate reduction was introduced by Turkevitch in 1951.[147] In this method, citrate was applied as a reducing agent and gold nanoparticles in the size of ca. 20 nm could be normally prepared in aqueous solution (Figure 1.9A). Moreover, Au NPs with different sizes from 16 to 147 nm could be synthesized by the same procedure as well by adjusting the ratio between reducing and stabilizing agents.[148,149] Currently, this method is often used to prepare Au NPs possessing a rather loose shell of ligands for further modification. On the other hand, the Brust-Schiffrin method was reported in 1994, in which a two-phase system (toluene/water) is needed (Figure 1.9B). Firstly, $AuCl_4^-$ is transferred to toluene phase by a phase-transfer reagent, e.g. tetraoctylammonium bromide. This gold salt is then reduced by $NaBH_4$ in the presence of a stabilizer such as an organic thiol compound.[44] By this method, Au NPs with diameters ranging from 1.5 to 5.2 nm are obtained. These nanoparticles can be readily handled and functionalized as normal organic molecules.[144] Furthermore, based on the above two methods, subsequent place-exchange reactions (Figure 1.9C) are another means developed for preparing the Au NPs with a mixed shell or with a targeting organic shell that contains functional groups, such as aldehydes and ketones, which are not compatible with the classic reduction condition.[151]

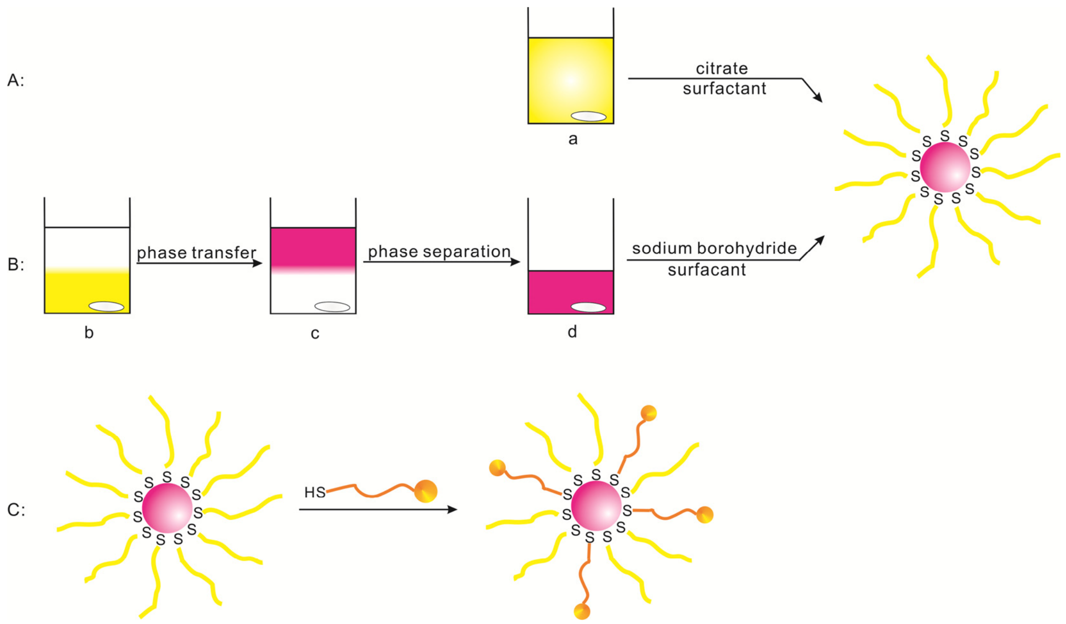


Figure 1.9. Schematic representation of gold nanoparticles synthesized by different methods. A: citrate reduction. a) Gold salt ($HAuCl_4$) in water. B: Brust-Schiffrin method. b) Two-phase system ($HAuCl_4$ in water and phase transfer agent in toluene); c) Gold colloids are transferred to the organic phase by the phase transfer agent. The toluene phase changes to red-wine color, while the aqueous solution changes to colorless; d) Organic phase is separated by extraction to inhibit the hydrolysis of $NaBH_4$ in the next step. C: place-exchange reaction for preparing mixed SAMs on Au NPs or Au NPs with an organic shell containing functional groups which are not compatible with the reducing agents.

Attempts to realize the photo-induced isomerization on surfaces of different chromophores, mainly from azobenzene, began at the end of the last century. In 1998, Evans et al.[152] managed to observe reversible photo-induced *Z*/*E* isomerization of an azobenzene derivative in mixed SAMs on a gold colloid that was synthesized by place-exchange reaction. However, only a small number of reversible switching cycles with low quantum yields were obtained due to significant aggregation and precipitation of Au NPs. Afterwards, Whitesell and his colleagues[153] investigated a relationship between the photoisomerization quantum yields of azobenzene molecules and the chain length in the system of alkanethiol-capped gold nanoparticles. It was found that the quantum yields markedly increased upon longer linker lengths, although they were still much lower than with the corresponding free thiols. The authors attributed these results to length-dependent quenching of the excited state by the metallic core and less free volume for isomerization of the azobenzene unit. In order to improve the photoisomerization efficiency, some optimized systems (Figure 1.10) with mixed SAMs fabricated by asymmetric disulfides (C_6H_{13}-azo-$OC_{12}H_{24}SSC_{12}H_{25}$)[154] or supramolecular complexes with cyclodextrin (CD) ($HSC_{10}H_{20}O$-azo + α-CD)[155] were designed. In the light of these successful approaches, applied research on the photo-induced isomerization of azobenzenes on Au NPs was carried out. So far, the control of salvation and precipitation of gold nanoparticles have already been achieved,[156] affording nanoparticle suprastructures *via* light-controlled self-assembly[157] and nanoparticle networks by varying the interparticle spacing.[158] Moreover, light-controlled molecular recognition,[159] photoswitchable catalysis,[160] and an invention of self-erasable and rewritable materials[161] have been realized as well.

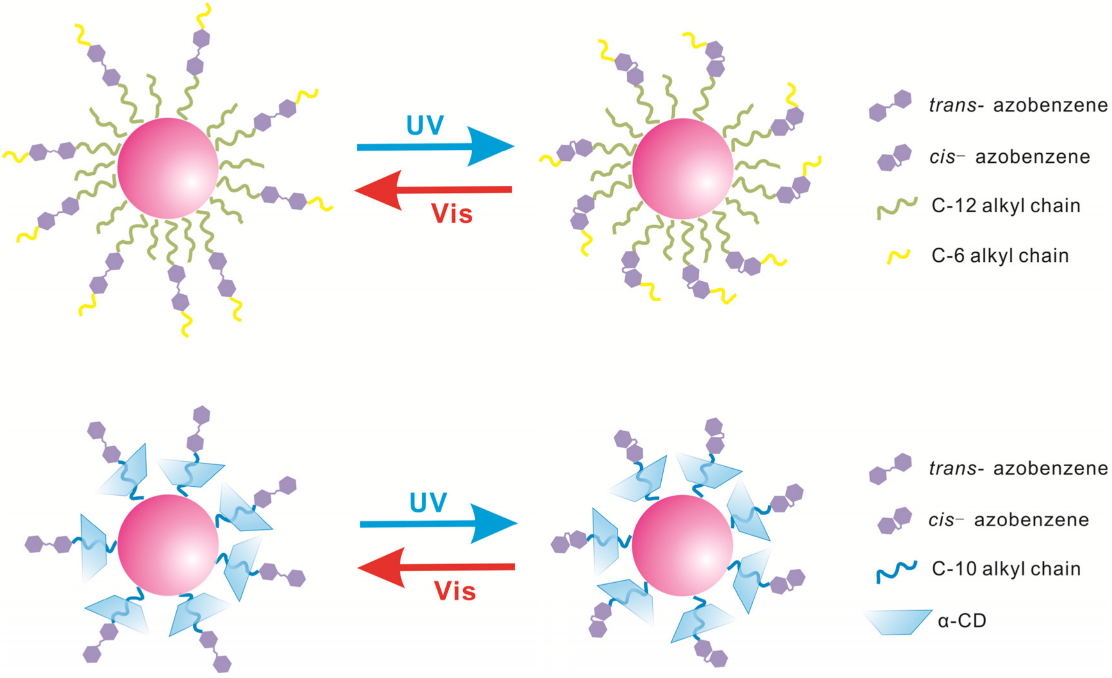


Figure 1.10. Idealized representation for the photoisomerization of azobenzene in the mixed SAMs fabricated by asymmetric disulfides (top)[154] and by supramolecular complexes with cyclodextrin (bottom).[155] Adapted with permission from reference

154. Copyright © 2003, American Chemical Society.

1.3.2 Planar Gold Surfaces

Compared to gold nanoparticles, the reversible photo-induced isomerization on planar gold surfaces, which lacks positive curvature, is even more difficultly managed due to steric hindrance of the isomerization in SAMs. So far, it has been recognized that an area of ~0.45-0.50 nm^2 per azobenzene unit is required for the efficient *trans*- to *cis*-isomerization in monolayers.[162] On the basis of this argument, scientists designed various azobenzene derivatives in order to increase the free volume between chromophores (Figure 1.11) and tested their photoresponsive capacities on gold surfaces, the results of which have been reviewed by Klajn.[163] Among these systems, the mixed SAMs made from an asymmetrical disulfide composed of an azobenzene and a short alkane thiolate (Figure 1.11a) is most popular. As a result, the surface density of azobenzene molecule is diluted, and enough free area of ~0.43 nm^2 for isomerization is acquired.[164-166] However, phase segregation of the two thiolates after annealing was observed, which could result in a reduced photoreactivity.[166] Therefore, asymmetrical sulfides[167-169] (Figure 1.11b) were used instead in some research because of their nondissociative adsorption process, but the disadvantage of the corresponding monolayers on gold was that they were less stable than with disulfides, which probably limited the development of these systems.

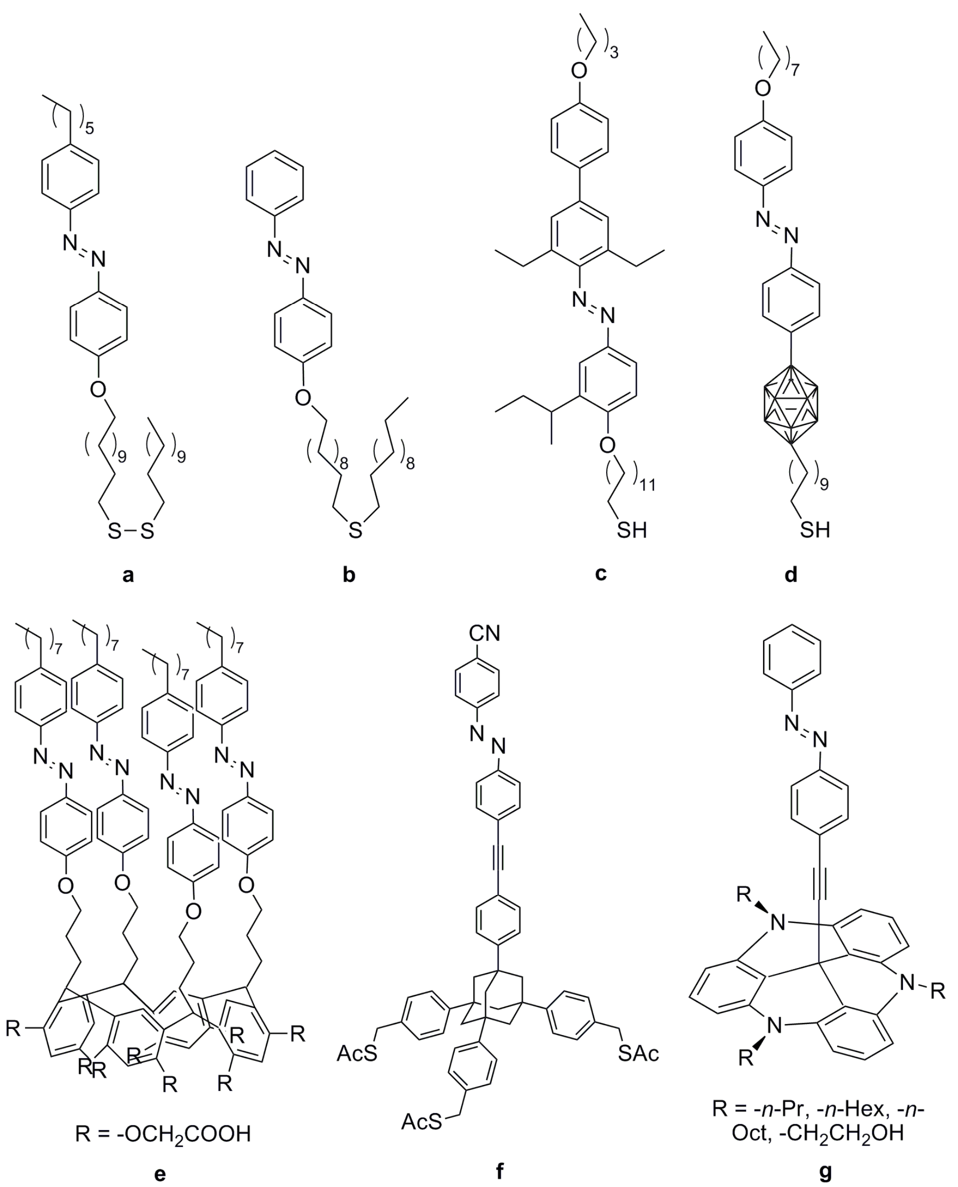


Figure 1.11. Chemical structures of different azobenzene surfactants designed to increase the free volume of azobenzene for photoisomerization.[163] **a**: asymmetric disulfide[164]; **b**: asymmetric sulfide[167]; **c**: alkylated azobenzene[166]; **d**: *p*-carborane incorporating azobenzene[172]; **e**: calix[4]resorcinarene-based azobenzene[173]; **f**: tripodal azobenzene[174]; **g**: triazatriangulenium carbocation-based azobenzene.[175]

Installing alkyl substituents on aromatic rings in azobenzene[166,170,171] (Figure 1.11c), as well as introducing a bulky group somewhere in the molecule[172] (Figure 1.11d) is another method to increase the free area of chromophores. Tamada et al.[166] modified azobenzenethiol and asymmetrical azobenzene disulfide by attaching a methyl group to the azobenzene ring. The isomerization efficiencies of these "methyl-functionalized" molecules on gold surfaces were comparable to that of non-functionalized molecules. It was found that the photoactivity of the methylated molecule was dramatically improved in the case of azobenzenthiol due to the steric effect of methyl group. On the other hand, in the case of asymmetrical azobenzene disulfide, the modified system revealed a similar photoresponse on the surface as the unmodified disulfides. Surprisingly, the SAMs prepared by methylated azobenzene disulfide still had a high photoreactivity even in the phase segregation produced after annealing. Modification of methyl groups on the azobenzene ring and the introduction of a bulky group in molecules are both beneficial for increasing the bulkiness of ligands. For example, Ito et al.[172] published that SAMs incorporated a three-dimensional cluster of *p*-carborane which exhibited a much higher and more reversible photochemical response than those without the *p*-carborane. Compared with the alkyl-substituted systems, the introduction of *p*-carborane was much more flexible and could be applicable for various other molecules.

In addition, utilization of bulky anchor groups or platforms, such as calix[4]resorcinarene[173] (Figure 1.11e), tripodal[174] (Figure 1.11f), and triazatriangulenium ions[175] (Figure 1.11g) can decrease the surface density of azobenzene units as well. The presence of these bulky anchor groups effectively inhibits adsorbate-substrate and adsorbate-adsorbate interactions, thus enabling the photo-induced switching.

It was well known that steric hindrance is a factor that influences the motion of neighboring molecular switches, it is, however, not the only one. Exciton coupling was corroborated as another factor restricting the photoswitching within a well ordered and closely packed SAMs.[176] In this research, Gahl et al. investigated the optical properties and geometric structure of SAMs of azobenzene functionalized alkanethiols and observed energetic shifts in optical reflection spectroscopy as a result of dipole-dipole interaction between the neighboring chromophores. Due to this exciton coupling, the optical excitation was quenched and thus the photo-induced isomerization in SAMs was hampered.[176]

Although the free volume of azobenzene plays a very important role in the photoisomerization process discussed above, it is likely that it only applies to monolayers of self-assembled azobenzene-derived alkane sulfur compounds. In 2007, Pace and his colleagues[177] successfully observed *E*/*Z* photoisomerization of a terminally thiolated azobiphenyl rigid rod molecule on gold surface by STM (Figure 1.12a). Interestingly, this switching occurred in a densely packed single-component SAM domain comprising hundreds of molecules. The authors attributed this photochemical response to a cooperative effect resulting from the rigidity of the aromatic backbone. Furthermore, the authors investigated the photoisomerization behavior of another methylated azobiphenyl derivative (Figure 1.12b), and attempted to unveil discrepancies between these two corresponding SAMs and to understand the steric effect of methyl groups in this rigid system.[178] Different from the tightly-packed SAMs in the first case, molecules in SAMs of the methylated azobiphenyl derivative were less organized and loosely packed, although both cases presented high photoisomerization efficiency (close to 100%) from the *trans*- to *cis*-state. The switching of "methyl-functionalized" molecules occurred individually in SAMs rather than a collective switching behavior.

Apart from the factors discussed above, end groups presenting on SAMs[165] and linker groups between the azobenzene moiety and the alkanethiol[179] influence the photoactivity of the chromophore on surfaces. In the light of these effective fundamental investigations, some successful systems have been put into practice, including light-triggered molecule adsorption,[168] DNA release,[169] cell adhesion,[180] surface wetting control,[181,182] and electron transfer.[183,184]

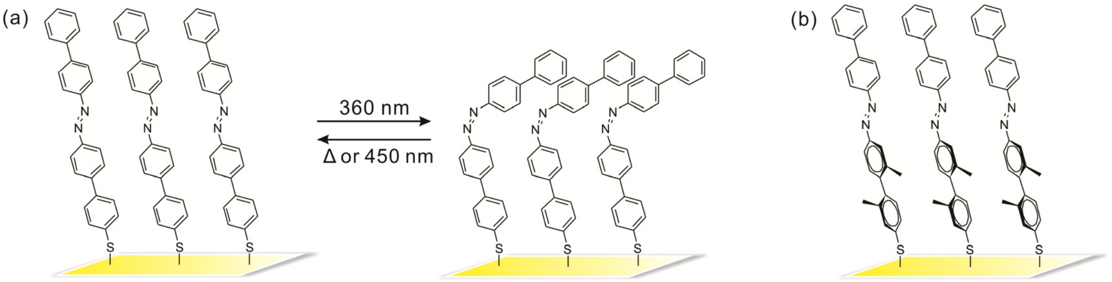


Figure 1.12. Schematic representation of (a) photo-induced isomerization of

azobiphenyl molecules on gold surface,[177] (b)methylated azobiphenyl derivative on gold.[178] Adapted with permission from reference 178. Copyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

2. SCIENTIFIC GOALS

The goal of this project is to carry out fundamental research on the reversible photo-induced *Z*/*E* isomerization of aromatic imines in solution and its corresponding photoactivity on gold surfaces.

As discussed in the Introduction (Section 1.2.2.2), the applications based on the photo-responsive property of stilbene could be limited due to the smaller energy discrepancy between two isomers, much higher energy barrier of thermal isomerization, and several side reactions, e.g., photodimerization and photocyclization of *cis*-stilbenen. On the other hand, although azobenzene (Section 1.2.2.1) is able to perform the reversible *Z*/*E* isomerization with higher isomerization efficiency, and no obvious by-product was observed, the slower thermal back reaction could also be problematic when the photo reaction is carried out on the surfaces.

In this work, conjugated imine derivatives have been chosen as the target system (Figure 2.1). Their reversible isomerization in solution will be investigated. An attempt to achieve the light-induced switching of the corresponding SAMs on gold surfaces will be conducted. However, the relatively low activation energy in the thermal relaxation process of the imine bond is sometimes problematic. Although it results in an extremely rapid reversible isomerization, in most cases the *cis*-isomers are too unstable at room temperature to be observed by most methods. Therefore, the characterization of *cis*-transition state still remains a challenging.

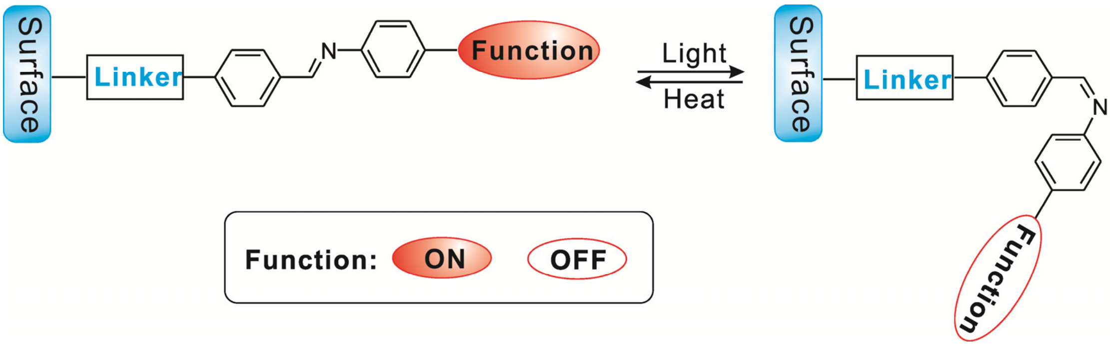


Figure 2.1. Schematic representation of modular imine-switches.

This thesis has the following objectives:

1. To synthesize several different aromatic thiol functionalized imines for SAM construction on gold surfaces. Due to the instability of free thiol in the presence of oxygen and the easier decomposition of imine under acidic conditions, purification of the final products should be carefully considered and performed.

2. To investigate reversible photo-induced isomerization of series of conjugated imine compounds in solution, e.g., *N*-benzylideneaniline. Solvent effects and substituent effects in these processes, especially for the thermal back reaction (from *Z* to *E*), should be better understood by NMR experiments and theoretical calculation.

3. To test photo-activities of imine switches in SAMs on gold nanoparticles. For this purpose, the corresponding gold nanoparticles will be synthesized by an optimized Brust-Schiffrin method.[154] Afterwards NMR measurements at low temperature will be performed to monitor the switching process. The isomerization efficiency of this system will be compared to those for the corresponding free thiol molecule and other azobenzene-modified gold nanoparticles.

4. To construct imine switches on gold planar surface by two different approaches, i.e., either by direct immobilization of the pre-synthesized free thiol molecules containing the imine groups on gold or in-situ imine formation on the surface-presenting amino-terminal groups. The produced SAMs will be characterized by IRRAS, XPS, NEXAFS, and contact angle measurement to examine the monolayer structure and molecular orientation. These measurements should also be performed for mixed SAMs prepared by in-situ imine hydrolysis. Finally, the photo-induced isomerizations of the normal SAMs and mixed SAMs will be studied by NEXAFS.

3. PUBLICATIONS

3.1 In-situ Formation and Detailed Analysis of Imine Bonds for The Construction of Conjugated Aromatic Monolayers on Au(111)

This chapter was published in the following journal:

Y. Luo, M. Piantek, J. Miguel, M. Bernien, W. Kuch, R. Haag, *Appl. Phys. A* **2008**, *93*, 293-301 (DOI: 10.1007/s00339-008-4824-4).
http://www.springerlink.com/content/20g0072611117w41/

3.2 Effective Reversible Photoinduced Switching of Self-Assembled Monolayers of Functional Imines on Gold Nanoparticles

This chapter was published in the following journal:

Ying Luo, Sergey Korchak, Hans-Martin Vieth, Rainer Haag, *ChemPhysChem*. **2011**, *12*, 132-135 (DOI: 10.1002/cphc.201000694).
http://onlinelibrary.wiley.com/doi/10.1002/cphc.201000694/abstract

3.3 *cis-trans* Isomerisation of Substituted Aromatic Imines: A Comparative Experimental and Theoretical Study

This chapter was published online in the following journal:

Ying Luo, Manuel Utecht, Jadranka Dokić, Sergey Korchak, Hans-Martin Vieth, Rainer Haag, Peter Saalfrank, *ChemPhysChem* **2011**, *12*, 2311-2321 (DOI: 10.1002/cphc.201100179).
http://onlinelibrary.wiley.com/doi/10.1002/cphc.201100179/abstract

3.4 In Situ Hydrolysis of Imine Derivatives on Au(111) for the Formation of Aromatic Mixed Self-Assembled Monolayers: Multitechnique Analysis of This Tunable Surface Modification

This chapter was published to the following journal:

Ying Luo, Matthias Bernien, Alex Krüger, Christian F. Hermanns, Jorge Miguel, Yin-Ming Chang, Simon Jaekel, Wolfgang Kuch, Rainer Haag, *Langmuir*, **2012**, *28*, 358-366 (DOI: 10.1021/la202696a).
http://pubs.acs.org/doi/abs/10.1021/la202696a

3.5 Imine Derivatives on Au(111): Evidence for "Inverted" Thermal Isomerization

This chapter was published in the following journal:

Johannes Mielke, Felix Leyssner, Matthias Koch, Stephan Meyer, Ying Luo, Sofia Selvanathan, Rainer Haag, Petra Tegeder, Leonhard Grill, *ACS Nano* **2011**, *5*, 2090-2097 (DOI: 10.1021/nn103297e).

http://pubs.acs.org/doi/abs/10.1021/nn103297e

4. SUMMARY AND CONCLUSION

In this thesis, several conjugated imine compounds, such as *N*-benzylideneaniline, and imine-functionalized free thiols were successfully synthesized. Their reversible photo-responsive *Z*/*E* isomerization has been investigated in detail in three different environments: in solution, in SAMs on convex surfaces of gold nanoparticles, and in SAMs on planar gold surfaces. In some cases, effective switching was finally achieved.

To better understand the reversible photo-induced isomerization process of imine molecules in solution, especially for the thermal back reaction, kinetic studies including substituent effects and solvent effects in *cis*- to *trans*-transitions of *N*-benzylideneaniline derivatives were performed experimentally and theoretically. According to the theoretical calculation, an inversion mechanism was speculated during this process. When an electron acceptor group, e.g., cyano group, was located at the *para*-position on the aniline ring, a perpendicular transition state (TS, β-β'$\approx 90^{o}$) (Figure 4.1) is favored, as suggested by Yamataka.[185] Meanwhile, the activation energy became lower and thus the corresponding *cis*-isomer decayed faster. In contrast, if an electron donor group, like a methoxyl group, was located at the *para*-position on the aniline ring instead, a transition state different from perpendicular TS was observed, but with a value of β-β' $\approx 60^{o}$. On the other hand, solvent effect does not obviously influence either reaction mechanism or activation energy as much as the substituent effect.

Furthermore, although with a similar trend, theoretical rates are typically two to five orders of magnitude larger than the experimental rates, which could be attributed to a simplified treatment of the solvent in the theoretical computations. Nevertheless, this study provides valuable information to identify “optimal” switches with good photochromicity and reasonable thermal stability.

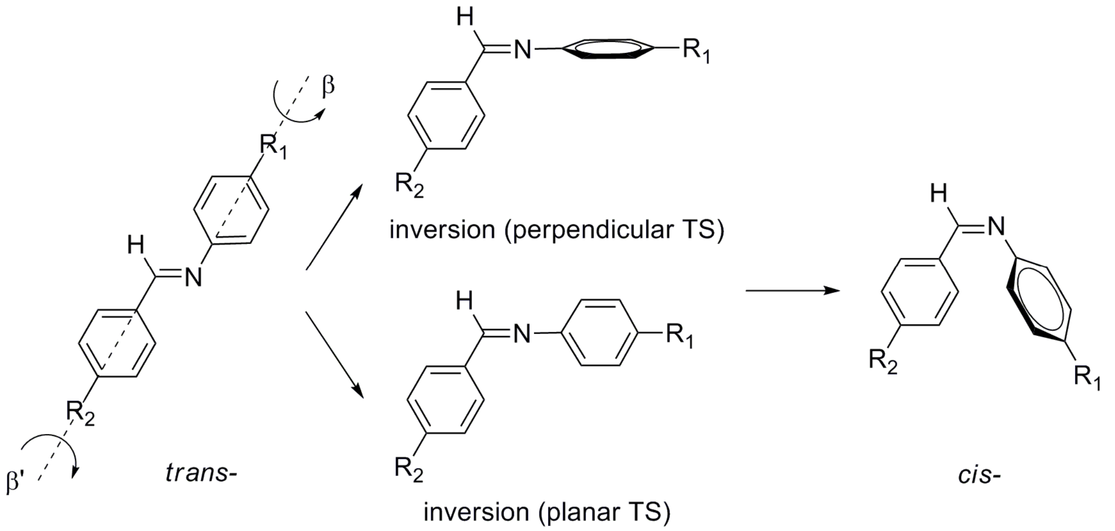


Figure 4.1. Two different transition states during the thermal isomerization of *N*-benzylideneaniline derivatives.[185]

In the second study, a novel gold nanoparticle coated by a self-assembled monolayer of a conjugated imine derivative was synthesized with satisfactory yield. These nanoparticles were characterized by transmission electron microscopy (TEM) and were confirmed to have an average diameter of 3.6 ± 0.9 nm with a relatively narrow size distribution range. The subsequent isomerization experiments demonstrated that the switching efficiency of this system reached up to 50%, which is comparable to free molecules under the same condition. Even after eight reversible isomerization cycles, no significant decomposition or aggregation was observed.

In order to achieve the *Z*/*E* isomerization on planar gold surfaces, on which an intermolecular distance in ordered SAMs is relatively smaller than that in SAMs on gold nanoparticles, it could be necessary to reduce the steric hindrance of the imine chromophore. The third part, therefore, concentrated on the construction of SAMs composed of imine functional groups on gold followed by the chemical modification of these monolayers to acquire more free volume for imine groups. Initially, amine terminated SAMs were formed by the direct fabrication of 4'-aminobiphenyl-4-thiol. However, there was only a small amount of orientation detected for this layer by near edge X-ray absorption fine structure (NEXAFS) measurements due to the interaction between amino group and gold surface. Although the following in-situ imine condensation of terminated amino group with different benzaldehyde derivatives was successful, this reaction was incomplete as a result of the limited order. Taking into account the disorder of molecules assembled on this layer, photoactivity investigation of this system is meaningless.

The alternative approach was performed in which a mixed SAM, via in-situ partial hydrolysis of monolayer on the gold surface coated by pre-synthesized free thiol molecules containing the imine groups, was prepared. This hydrolysis reaction was accomplished either in chloroform or in acetic acid aqueous solution with a pH value of 3. Surface densities of two components could be controlled to some extent based on the reaction time. Moreover, XPS and NEXAFS results suggested that the surface quality and the molecular orientation were well maintained during this process. Unfortunately, a preliminary photoswitching test was failed.

In conclusion, it has been corroborated that imine derivatives with different terminal groups could be well fabricated on not only gold nanoparticles but also planar gold surfaces. Additionally, a novel approach taking advantage of in-situ hydrolysis of imine double bond was introduced successfully to construct the mixed SAMs consisting of two components with the controllable surface densities. Although switching of such dilute SAMs still remains a challenge a rapid and effective reversible photo-induced switching process was shown on gold nanoparticles, which might have a potential application in the design of switchable surface properties. Furthermore, the fundamental research about thermal relaxation of imine compounds beneficial for further optimization the switching system and thus for a better achieving of the photoisomerization on the surfaces more effectively.

5. OUTLOOK

Since the mixed SAMs consisting of two components, imine compounds and amine produced by the hydrolysis, with the different surface density have been successfully established, further tests about the photo-induced isomerization of these systems should be carried out in the future. The chromophore density depended photoactivities could also be detailed surveyed.

It has been shown that the *cis*-isomer of imine compound is only stable at low temperature due to the far smaller activation energy of thermal back reaction, which could limit its practical application. Thereby, further modifications of imine compounds are essential to improve their stabilities under ambient conditions and meanwhile to provide better photochromicities.

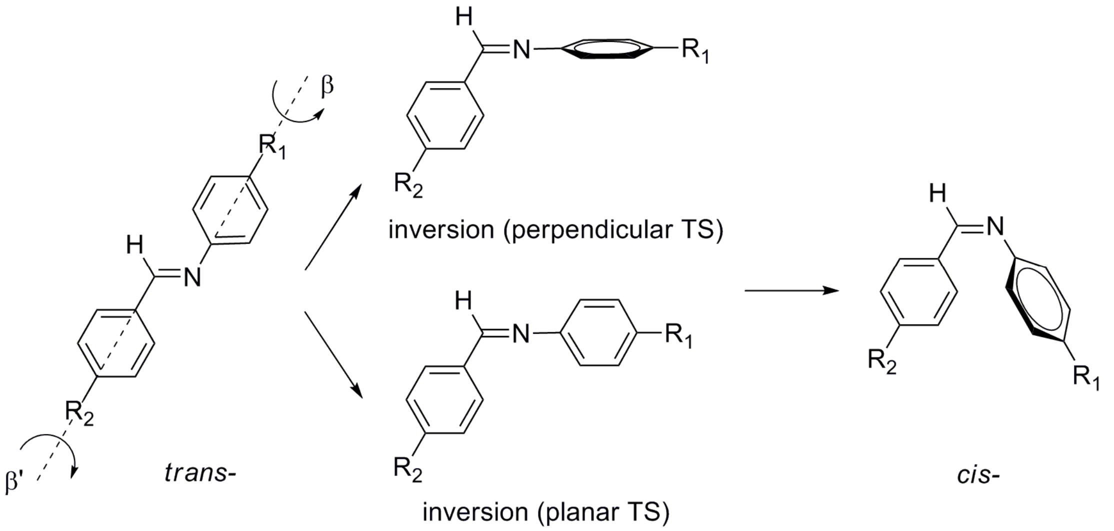
Furthermore, like imine, oxime ether and hydrazone possess C=N double bonds and can undergo the reversible photo-induced isomerization as well. Designs, syntheses, and photoactivity evaluations of these alternate systems could be of interest.

6. ZUSAMMENFASSUNG

In dieser Doktorarbeit wurden verschiedene konjugierte Iminverbindungen wie N-benzylidenanilin und iminfunktionalisierte Thiole erfolgreich dargestellt. Deren reversible lichtinduzierte *Z/E* Isomerisierung wurde detailliert in drei unterschiedlichen Systemen (Lösung, in SAMs auf konvexen Oberflächen auf Goldnanopartikel und in SAMs auf planaren Goldoberflächen) untersucht. In einigen Fällen konnte ein effektives Schalten gezeigt werden.

Um den Prozess, vor allem die thermische Rückreaktion, der lichtgesteuerten Isomerisierung von Iminen besser zu verstehen, wurden kinetische Studien bezüglich Substituenten- und Lösungsmitteleffekte der *Cis* zu *Trans* Übergänge von N-benzylidenanilin sowohl experimentell als auch theoretisch durchgeführt. Den theoretischen Berechnungen zufolge wurde über einen Inversionsmechanismus des Prozesses spekuliert. Befand sich eine Elektronen-Akzeptor-Gruppe wie die Cyanogruppe in der para-Position des Anilinrings ist nach Yamataka ein rechtwinkliger Übergangszustand (ÜZ, β-β'$\approx 90^{o}$) bevorzugt (Abbildung 6.1).[185] Währenddessen sank die Aktivierungsenergie, was zu einer schnelleren Abnahme des korrespondierenden *cis*-Isomeres führte. Im Gegensatz dazu resultiert ein Elektronendonor, wie die Methoxygruppe, in para-Position des Anilinrings zu einem anderen, nicht rechtwinkligen, ÜZ mit einem Winkel von β-β' $\approx 60°$. Auf der anderen Seite beeinflussen Lösungsmitteleffekte augenscheinlich nicht den Reaktionsmechanismus oder die Aktivierungsenergie in dem Maße wie Substituenteneffekte.

Desweiteren zeigen theoretisch berechnete Raten einen ähnlichen Trend, typischerweise liegen sie aber um zwei bis fünf Größenordnungen über den experimentellen Daten, was an der vereinfachten Betrachtung des Lösungsmittels in den theoretischen Berechnungen liegen kann. Trotzdem liefert diese Studie wertvolle Information um einen optimalen Schalter mit guter Photochromie und angemessener thermischer Stabilität zu erhalten. Der Trend für funktionalisierte Systeme wurde richtig wiedergegeben.



Abildung 6.1. Zwei verschiedene Übergangszustände während der thermischen Isomerisierung von N-benzylidenanilinderivaten.[185]

In der zweiten Untersuchung wurden neuartige Goldnanopartikel beschichtet mit einer selbstorganisierten Monolage konjugierter Iminderivate mit einer guten Ausbeute synthetisiert. Diese Nanopartikel wurden mittels Transmissionselektronenmikroskopie (TEM) charakterisiert und zeigten einen durchschnittlichen Durchmesser von 3.66 ± 0.9 nm mit einer relativ kleinen Größenverteilung. Die folgenden Isomerisierungsexperimente zeigten eine Schalteffizienz von 50%, was vergleichbar mit freien Molekülen unter den gleichen Bedingungen ist. Selbst nach acht reversiblen Isomerisierungszyklen wurde keine signifikante Zersetzung oder Aggregation beobachtet.

Um die *Z*/*E* Isomerisierung auf planaren Goldoberflächen zu erreichen, ist es aufgrund des kleineren zwischenmolekularen Abstandes in geordneten SAMs im Vergleich zu SAMs in Goldnanopartikeln notwendig den sterischen Anspruch der Iminchromophore zu reduzieren. Daher konzentrierte sich der dritte Teil dieser Doktorarbeit mit der Konstruktion von SAMs aufgebaut aus Imingruppen auf Gold gefolgt von der chemischen Modifizierung dieser Monolagen um mehr freies Volumen für die Imingruppen zu schaffen. Zuerst wurden aminterminierte SAMs durch die direkte Herstellung mit 4'-Aminobiphenyl-4-thiol gebildet. Jedoch wurde nur eine geringe Orientierung dieser Schicht durch Röntgen Nahkanten Absorptions

Spektroskopie (NEXAFS) detektiert, was sich auf die Wechselwirkung der Aminogruppe mit der Goldoberfläche zurückführen lässt. Obwohl die nachfolgende in-situ Iminkondensation der terminalen Aminogruppe mit verschiedenen Benzaldehydderivaten erfolgreich war, war die Reaktion aufgrund der begrenzten Ordnung unvollständig. Berücksichtigt man jedoch die Unordnung der Moleküle in der Monolage sind Untersuchungen der Photoaktivität bedeutungslos.

Ein alternativer Ansatz, der hier durchgeführt wurde, beinhaltet die teilweise in-situ Hydrolyse gemischter SAMs bestehend aus vorher synthetisierten freien Thiolen mit Imingruppen. Die Hydrolyse wurde mit Chloroform und in wäßriger Essigsäure (pH Wert = 3) durchgeführt. Die Oberflächendichten beider Komponenten konnte in einem gewissen Maß über die Reaktionszeit kontrolliert werden. Desweiteren zeigten XPS und NEXAFS Daten, dass die Qualität der Oberfläche und die Orientierung der Moleküle während des Prozesses erhalten blieben. Unglücklicherweise schlug das lichtinduzierte Schalten fehl.

Zusammenfassend wurde bestätigt, dass Iminderivate mit unterschiedlichen Endgruppen nicht nur auf Goldnanopartikeln sondern auch auf planaren Goldoberflächen hergestellt werden konnten. Zusätzlich ist ein neuer Ansatz etabliert worden, der erfolgreich die Vorteile der in-situ Hydrolyse von der Imindoppelbindung ausnutzt, um gemischte SAMs bestehend aus zwei Komponenten mit kontrollierbaren Oberflächendichten zu konstruieren. Obwohl ein Schalten solch verdünnter Oberflächen immer noch eine Herausforderung ist, wurde ein schneller, effektiver und reversibler licht-induzierter Schaltprozess auf Goldnanopartikeln gezeigt, was potenzielle Anwendung im Design schaltbarer Oberflächeneigenschaften haben kann.

Desweiteren erweist sich die grundlegende Erforschung der thermischen Relaxation von Iminderivaten vorteilhaft für die weitere Optimierung schaltbarer Systeme und daher für eine Steigerung der Effektivität der Photoisomerisierung auf Oberflächen.

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8. PUBLICATIONS AND PRESENTATIONS

Publications

11. **Ying Luo**, Matthias Bernien, Alex Krüger, Christian F. Hermanns, Jorge Miguel, Yin-Ming Chang, Simon Jaekel, Wolfgang Kuch, Rainer Haag, *In Situ Hydrolysis of Imine Derivatives on Au(111) for the Formation of Aromatic Mixed Self-Assembled Monolayers: Multitechnique Analysis of This Tunable Surface Modification,* Langmuir **2012**, *28*, 358-366.

10. **Ying Luo**, Manuel Utecht, Jadranka Dokić, Sergey Korchak, Hans-Martin Vieth, Rainer Haag, Peter Saalfrank, *cis-trans Isomerization of Substituted Aromatic Imines: A Comparative Experimental and Theoretical Study*, ChemPhysChem **2011**, *12*, 2311-2321.

9. Johannes Mielke, Felix Leyssner, Matthias Koch, Stephan Meyer, **Ying Luo**, Sofia Selvanathan, Rainer Haag, Petra Tegeder, Leonhard Grill, *Imine Derivative on Au(111): Evidence for "Inverted" Thermal Isomerization*, ACS Nano **2011**, *5*, 2090-2097.

8. **Ying Luo**, Sergey Korchak, Hans-Martin Vieth, Rainer Haag, *Effectively Reversible Photo-induced Switching of Self-Assembled Monolayers of Functional Imines on Gold Nanoparticles*, ChemPhysChem **2011**, *12*, 132-135.

7. László Óvári, **Ying Luo**, Felix Leyssner, Rainer Haag, Martin Wolf, Petra Tegeder, *Adsorption and switching properties of a N-benzylideneaniline based molecular switch on a Au(111) surface*, J. Chem. Phys. **2010**, *133*, 44707.

6. Sebastian Hagen, **Ying Luo**, Rainer Haag, Martin Wolf, Petra Tegeder, *Electronic structure and electron dynamics at an organic molecule/metal interface: interface states of tetra-tert-butyl-imine/Au(111)*, New Journal of Physics **2010**, *12*, 125022.

5. U. Kemelbekov, **Y. Luo**, Z. Orynbekova, Zh. Rustembekov, R. Haag, W. Saenger, K. Praliyev, *IR, UV and NMR Studies of β-Cyclodextrin Inclusion Complexes of*

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4. Shangjie Xu, **Ying Luo**, Ralph Graeser, André Warnecke, Felix Kratz, Peter Hauff, Kai Licha, Rainer Haag, *Development of pH-Responsive Core-Shell Nanocarriers for Delivery of Therapeutic and Diagnostic Agents*, Bioorganic & Medicinal Chemistry Letters **2009**, *19*, 1030-1034.

3. **Ying Luo**, Marten Piantek, Jorge Miguel, Matthias Bernien, Wolfgang Kuch, Rainer Haag, In-situ *Formation and Detailed Analysis of Imine Bonds for The Construction of Conjugated Aromatic Monolayers on Au(111)*, Appl. Phys. A **2008**, *93*, 293-301.

2. Shangjie Xu, **Ying Luo**, Rainer Haag; *Structure-Transport Relationship of Dendritic Core-Shell Nanocarriers for Polar Dyes*, Macromolecular Rapid Communications **2008**, *29(2)*, 171-174.

1. Shangjie Xu, **Ying Luo**, Rainer Haag; *Water-Soluble pH-Responsive Dendritic Core-Shell Nanocarriers for Polar Dyes Based on Poly(ethylene imine)*, Macromolecular Bioscience **2007**, *7(8)*, 968-974.

Poster Presentations

5. 7th. Deutsches BioSensor Symposium (3-6 April 2011, Heilbad Heiligenstadt, Germany)

Poster: Controllable Formation of Mixed Self-Assembled Monolayers via Hydrolysis of Imine on Au(111); Ying Luo, Matthias Bernien, Alex Krüger, Felix Hermanns, Wolfgang Kuch, Rainer Haag

4. Faraday Discussion 143 – Soft Nanotechnology (15-17 June 2009, London, United Kingdom)

Poster: Photo-induced Switchable Gold Nanoparticles Based on Imine Derivatives; Ying Luo, Sergey Korchak, Hans-Martin Vieth, Rainer Haag

3. SFB Conference – Molecular Switches: Elementary Processes and Applications

(27-29 May 2009, Salzau, Germany)

Poster: Molecular Switches on Surfaces Based on Conjugated Imine Compounds; Ying Luo, Rainer Haag

2. Polydays 2008 – Active and Adaptive Polymeric Materials (1-2 October 2008, Berlin, Germany)

Poster: Development of pH-Responsive Core-Shell Nanocarriers for Delivery of Therapeutic and Diagnostic Agents; Ying Luo, Shangjie Xu, Ralph Graeser, André Warnecke, Felix Kratz, Peter Hauff, Kai Licha, Rainer Haag

1. 7th. International Symposium on Polymer Therapeutics: From Laboratory to Clinical Practice (26-28 May 2008, Valencia, Spain)

Poster: Development of pH-Responsive Core-Shell Nanocarriers for Delivery of Therapeutic and Diagnostic Agents; Ying Luo, Shangjie Xu, Ralph Graeser, André Warnecke, Felix Kratz, Peter Hauff, Kai Licha, Rainer Haag.

9. CURRICULUM VITAE

For reasons of data protection, the Curriculum vitae is not published in the online version.