

3.8.10 Chemisorption of polyatomic chain-like hydrocarbons on metals and semiconductors

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3.8.10.1 Introduction

Long chain hydrocarbons of defined length can adsorb on metal or semiconductor surfaces from solution or the gas phase to form regularly arranged, well-ordered films which are called self-assembled monolayers (SAMs). Constituents of molecules forming self-assembled monolayers are the anchor group that chemically attaches the chains to the substrate, the chain or linker group, and the tail group on the terminus which determines wettability and chemical reactivity of the monolayer.

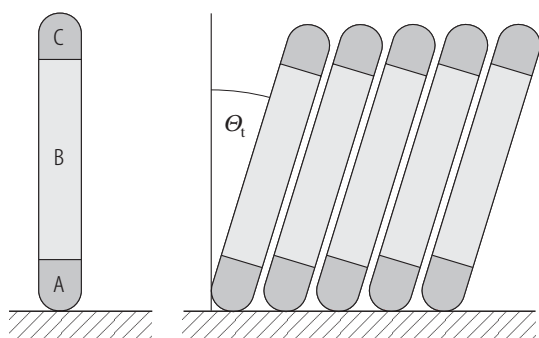


Fig. 1. The constituents of a self-assembled monolayer can be split into three components: An anchor group A, a spacer group or chain B and a tail group C. SAMs are ordered assemblies of such molecules on flat surfaces whose components are tilted by an angle θ_t from the surface normal.

Such highly ordered, stable monolayers may have applications in diverse areas such as wetting control, corrosion inhibition [97Sch], adhesion promotion [97Kim], [99Kid], the preparation of biocompatible surfaces [91Pri] or the modification of electronic surface properties [97Cam]. SAMs can also be used for lateral structuring of surfaces, e.g. by microcontact printing [98Del], [99Kum] or electron beam lithography [01Göl]. Since SAMs can be very easily prepared from solution, they present a straightforward way to modify physical and chemical properties of a surface by proper choice of their chemical constitution. Several reviews and books on the preparation, structure and properties of SAMs have appeared in the literature [91Ulm], [96Ulm], [98Ulm], [00Sch], [01Fen], [01Ulm], [01Zha] and a large number of spectroscopic, scattering and imaging methods have been applied for their structural characterization.

3.8.10.2 Physical and Chemical Properties

3.8.10.2.1 Structural data: Tilt and twist angles, packing and lattice structures

The main numerical values to characterize packing and structure of self-assembled monolayers on a given substrate are the tilt and twist angles of the chains which are tabulated in table 1.

The tilt of the chains in a self-assembled monolayer originates from the requirement to fill volume and to maximize interchain van der Waals interactions. It decreases with lower packing density, e.g. alkanethiols on gold (111) are more strongly tilted than alkanethiols on silver (111) due to the higher packing density on gold (see table 1). At a given chain length, the thickness of the monolayer can be calculated from the tilt angle.

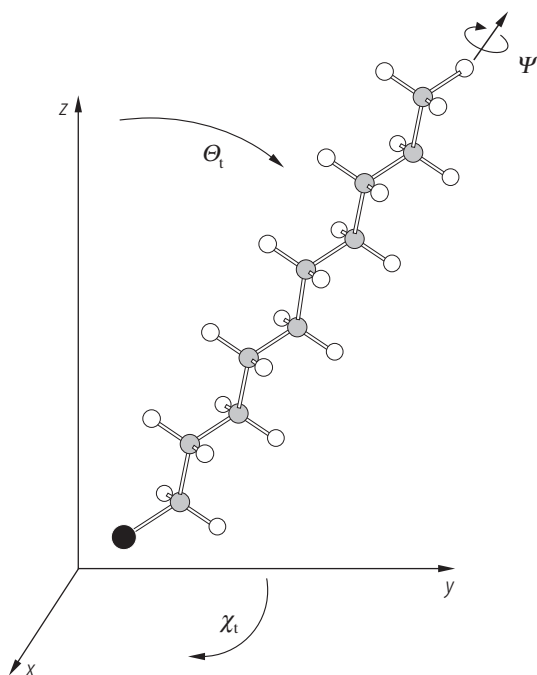


Fig. 2. Eulerian angles that describe the orientation of an alkane chain in a self-assembled monolayer: θ_t is the tilt angle of the chain with respect to the surface normal; ψ is the twist angle of the chain which defines the rotation of the alkyl carbon backbone about the chain axis with respect to the plane defined by this axis and the surface normal. χ_t is the azimuthal rotation around the z-axis with respect to the substrate lattice and has rarely been determined experimentally; [00Sch].

For the determination of tilt and twist angles, spectroscopic techniques such as X-ray Photoelectron Spectroscopy (XPS), Infrared Reflection Absorption Spectroscopy (IRAS) or Near Edge X-ray Absorption Fine Structure (NEXAFS) have been used, and imaging methods such as Scanning Tunneling Microscopy (STM) or Atomic Force Microscopy (AFM) provide a real space representation of the structure and homogeneity of SAMs. Scattering methods such as Low Energy Electron Diffraction (LEED), Grazing Incidence X-ray Diffraction (GIXD) and Low Energy Atom Diffraction (LEAD) provide direct information about the two-dimensional structure of SAMs, i.e., their structure projected onto the surface plane. Both scattering and spectroscopic methods are spatially averaging, however, the averaging is performed over different regions with different weight. The molecular tilt angle determined by IRAS or NEXAFS, e.g., is averaged over all molecular chains, including disordered regions such as grain boundaries or defect sites. Note, that NEXAFS probes the molecular orientation at the SAM surface (due to the limited electron mean free path) [98Tho], whereas IRAS measurements give the average angles over the whole film thickness. In contrast, the determination of the tilt angle by GIXD includes only ordered and crystalline regions. This is important when results from different techniques are compared. Since the values reported in table 1 may differ slightly from method to method for a specific substrate/anchor group/chain combination, the applied technique has been indicated in each case. For a precise determination of tilt and twist angles by IRAS, it has been reported recently that effects such as the grain size of the substances used for bulk reference spectra have to be taken into account [01Arn].

In this compilation of published data on SAMs, aliphatic and aromatic hydrocarbons and their terminally substituted derivatives are tabulated. In table 1, only systems that form well-ordered aggregates are included. For aliphatic chains, only data for chain lengths of 16 or more carbon atoms are listed, since routinely reproducible values of the tilt and twist angles are obtained only for these highly ordered films, whereas smaller chain lengths may lead to disordered or unstable systems. For aromatic systems, data for biphenyl and terphenyl containing SAMs have been tabulated. The twist angles of the chains have only been determined for a few systems and are included in table 1, when available. In most cases, these values have not been determined on single crystals, but on evaporated metal surfaces that contain small crystals with a predominant lattice orientation. In the few cases where no substrate orientation is given in table 1, SAMs on oxidic surfaces without regular orientation are concerned or no lattice orientation has been indicated in the primary literature. The two-dimensional structure of a SAM (i.e., the structure projected onto the surface plane) describes the type of crystalline long-range order, the symmetry, the lattice parameters and the packing in the plane. For some cases (e.g. alkanethiols on Au(111)), the unit cell may

contain several non-equivalent molecules. Superlattice structures are included in table 1, when data are available. Most of the data listed have been determined using SAMs prepared from dilute solution. Upon preparation from the gas phase, the growth kinetics of a SAM are usually faster due to the absence of solvent interactions, but the final, densely packed equilibrium structures are identical. Many spectroscopic investigations have been done in UHV and little or no structural differences are observed when compared to studies conducted under solvent, except for the terminal groups of the SAM. SAMs on nanoparticle surfaces (see table 3) have not been included in table 1, since these layers are usually more disordered than on flat single- or polycrystalline surfaces due to the particle curvature. All data given in table 1 have thus been determined on flat surfaces.

3.8.10.2.2 Heat of formation and thermal stability

As opposed to purely physisorbed systems, self-assembled monolayers are chemisorbed on the underlying surface and form stable covalent bonds between the anchor group and the substrate. The heat of chemisorption, which can be usually measured as the heat of desorption, is in many cases (especially for short chain lengths) equivalent to the enthalpy of formation of the anchor group-substrate bond (ca. 126 kJ/mol for alkanethiols on gold). As is shown in Fig. 3, only for longer chains ($n > 14$) a further contribution to the heat of desorption from van der Waals interactions between the chains is observed.

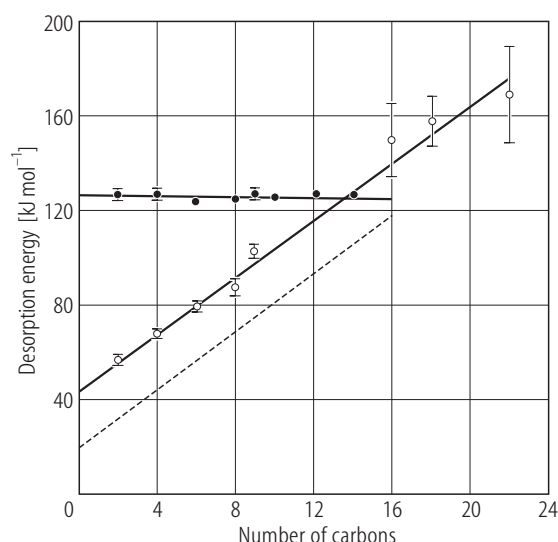


Fig. 3. Chemisorption (full symbols) and physisorption enthalpies (open symbols) for various alkanethiols on Au(111) as a function of the number of carbon atoms. For comparison, physisorption values for simple alkanes are indicated as dashed line. Only for chain lengths higher than 14 carbon atoms, the desorption energy is higher than the bond enthalpy of the anchor group-substrate bond. Values have been determined by temperature programmed desorption in UHV; [98Lav].

Since SAMs are covalently anchored on the substrate, they show higher resistance to desorption than physisorbed systems. Thermal desorption of alkanethiols on gold (111) occurs only at temperatures of about 500 K and this temperature is largely independent of the chain length [98Lav]. Trichlorosilane- or trialkoxysilane-based SAMs on oxide surfaces are thermally extremely stable due to the polymeric siloxane network formed on the surface. SAMs formed from octadecyltrichlorosilane on silicon dioxide have been found to be stable in UHV up to temperatures of 740 K, at which temperature the C-C bonds in the molecular backbone start to decompose [97Klu]. The siloxane network of the anchor groups remains on the surface after decomposition of the monolayers up to about 1100 K. Monolayers formed by reaction of 1-alkenes with hydrogen-terminated silicon surfaces have been reported to be stable up to 615 K [97Sun].

3.8.10.2.3 Wettability

The wettability of self-assembled monolayers is mainly determined by the chemical nature of their terminal group exposed to the surface. In table 2, a survey of advancing contact angle values of water and hexadecane is given for different end groups of SAMs. Generally, for densely packed and well-ordered monolayers and for a given backbone, the wettability is only weakly dependent on the substrate and the packing density. In table 2, only values for SAMs on gold have been listed. The contact angle increases with higher roughness of the substrate; table 2 lists only the limiting values for minimally rough evaporated surfaces. Aromatic SAMs show a smaller variation of the contact angle for different terminal groups since the aromatic backbone delocalizes induced charges, in contrast to aliphatic chains which present more localized terminal dipoles.

3.8.10.2.4 Anchor groups for SAMs on inorganic substrates

A broad variety of anchor groups have been used for the covalent attachment of hydrocarbon chains to inorganic surfaces and have been listed in table 3. On noble metals, sulfur containing anchor groups such as thiolates or disulfides which form covalent bonds to the surface are frequently utilized. On metal oxide surfaces, coordinative bonding to the metal ion component of the surface oxide via functional groups such as phosphonic or carboxylic acids often prevails. For most types of metal and semiconductor oxide surfaces, trialkoxysilanes or trichlorosilanes are versatile anchor groups that form two-dimensional cross-linked siloxane networks on the surface, but the long-range order of these SAMs is generally lower than that of e.g. alkanethiols on noble metals. As opposed to most of the other anchor groups listed in table 3, silanes require a minimum of water content in the solvent used for SAM formation in order to polymerize on the surface.

For particle (colloid) surfaces, the same anchor groups as for planar surfaces can in general be used. In table 3, data are included for anchor groups on nanoparticles in a size range from some nanometers to several hundred nanometers. Anchor groups for SAMs can also be used for the chemical attachment of thicker, more disordered films on a surface such as oligomeric or polymeric systems and are therefore of technological importance e.g. for adhesion improvement.

3.8.10.3 List of abbreviations

AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscopy
ATR-IR	Attenuated Total Reflection Infrared
GIXD	Grazing Incidence X-ray Diffractometry
IRAS	Infrared Reflection Absorption Spectroscopy
LEAD	Low Energy Atom Diffraction
LEED	Low Energy Electron Diffraction
NEXAFS	Near Edge X-ray Absorption Fine Structure
SAM	Self-assembled Monolayer
SPS	Surface Plasmon Spectroscopy
SPR	Surface Plasmon Resonance
STM	Scanning Tunneling Microscopy
UHV	Ultrahigh Vacuum
XANES	X-ray Absorption Near Edge Structure
XPS	X-ray Photoelectron Spectroscopy
XR	X-ray Reflectivity

3.8.10.4 Tables

Table 1. Tilt and twist angles, areas per molecule, structures and superlattices of self-assembled monolayers on various substrates.

System	Tilt angle	Twist angle	Area per molecule	Structure	Superlattice
Alkanethiol / Au(111)	32-34° (IRAS) [90Nuz1], [90Nuz2] 35° (NEXAFS) [92Häh]	55° (IRAS) [90Nuz1]	21.6 Å ² [00Sch]	(√3×√3)R30° [88Str], [90Chi]	c(4×2) LEAD [93Cam] GIXD [93Fen] STM [94Poi], [94Del], [94Buc] 6×√3 (STM, after 6 months storage) [02Noh]
Alkanethiol / oxidized Au(111)	18° (deposition from solution) 28° (vapour deposition) (NEXAFS) [99Yan]				
Alkanethiol / Au(111) exposed to Hg vapor	11° (IRAS) [98Tho] 26° (NEXAFS) [98Tho]	45° (IRAS) [98Tho]			
Dialkylsulfide / Au(111)				(√3×√3)R30° [99Sch]	
Alkaneselenol / Au(111)	15° (GIXD) [92Sam]				
Alkanethiol / Au(001)	33.5° (LEAD, GIXD) [95Li]		22.2 Å ² (LEAD, GIXD) [95Li]		as deposited: c(2×2) (LEED) [93Dub] annealed: c(2×8) (LEAD) [95Li]
Alkanethiol / Au(110)			23.5 Å ² (LEAD) [93Cam]		c(2×2) (LEAD) [93Cam]
OH-terminated Alkanethiol / Au(111)	28° (IRAS) [90Nuz2] 39.6° (NEXAFS, XPS) [97Dan]	50° [90Nuz2]			
HS(CH ₂) ₁₅ COOH / Au(111)	32° [90Nuz2]	55° [90Nuz2]		(√3×√3)R30° [90Nuz2]	
HS(CH ₂) ₁₅ CONH ₂ / Au(111)	31° [90Nuz2]	55° [90Nuz2]			
HS(CH ₂) ₁₆ CN / Au(111)	42.5° (NEXAFS) [03Fre]				
F(CF ₂) ₁₀ (CH ₂) _n -SH (n = 2,6,11) / Au(111)	0-16° (fluorinated segment, SPR, AFM) [01Tam]				p(2×2) or c(7×7) [01Tam]
F(CF ₂) ₁₀ (CH ₂) _n -SH (n = 2,11,17) / Au(111)	32-38° (alkyl segment, NEXAFS) 12.5-24° (fluorinated segment, XPS, IRAS, NEXAFS) [00Zha], [00Fre]	54-58° (alkyl segment) [00Zha]			
HS(CH ₂) ₁₁ (OCH ₂ CH ₂) ₃ OMe / Au(111)	~30° (alkyl segment) ~0° (oligoether segment, IRAS) [98Har]				
HS(OCH ₂ CH ₂) ₆ C ₁₀ H ₂₁ / Au(111)	32° (alkyl segment) ~0° (oligoether segment, IRAS) [98Van]	-30° [98Van]			

System	Tilt angle	Twist angle	Area per molecule	Structure	Superlattice
1,1'-Biphenyl-4-thiol / Au(111)	23° ± 5 (NEXAFS) [01Fre]	32° [01Fre]			
1,1':4',1''-Terphenyl-4-thiol / Au(111)	20° ± 5 (NEXAFS) [01Fre]	32° [01Fre]			
CH ₃ (C ₆ H ₄) ₂ SH / Au(111)	19° (GIXD) [00Leu]			(√3×√3)R30° [00Leu]	
CH ₃ (C ₆ H ₄) ₂ (CH ₂) _n SH (n = 1-6) / Au(111)	45 ± 10 (n = even) 23 ± 7 (n = odd) NEXAFS, IRAS [01Ron], [00Zha]	61 ± 10 (NEXAFS, IRAS) [01Ron], [00Zha]		(√3×√3)R30° (n = odd) [01Ron]	
Alkanethiol / Ag(111)	10° (NEXAFS) [98Him] 0-18° (SPS) [97Ehl] 12-13° (IRAS) [91Lai], [91Wal] 0° ± 5 (GIXD) [96Sam]		18.5 Å ² [00Sch]	(√3×√3)R10.9° [00Sch]	
HS(CH ₂) ₁₆ CN / Ag(111)	29.5° (NEXAFS) [03Fre]				
1,1'-Biphenyl-4-thiol / Ag(111)	18° ± 5 (NEXAFS) [01Fre]	32° [01Fre]			
1,1':4',1''-Terphenyl-4-thiol / Ag(111)	16° ± 5 [01Fre]				
CH ₃ (C ₆ H ₄) ₂ (CH ₂) _n SH (n = 1-6) / Ag(111)	24° ± 6 (n = even) 42° ± 9 (n = odd) NEXAFS, IRAS [01Ron]	54° ± 10 (NEXAFS, IRAS) [01Ron]			
HS(CH ₂) ₁₁ (OCH ₂ CH ₂) ₃ OMe / Ag(111)	~10° (alkyl segment) ~0° (oligoether segments, IRAS) [98Har]				
F(CF ₂) ₁₀ (CH ₂) _n -SH (n = 2,11,17) / Ag (111)	10-12° (alkyl segment, NEXAFS) 12.5-24° (fluorinated segment, XPS, IRAS, NEXAFS) [00Zha], [00Fre]	47-48° (alkyl segment) [00Zha]			
Alkanethiol / Hg	0° [96Mag], [98Ulm]				
Alkanethiol / Cu(111)	12° (IRAS) [91Lai] 12° (NEXAFS) [98Ima], [97Rie]		17.0 Å ² [91Lai]		
Alkanethiol / Fe	0° (XPS, AES) [90Str]				
Alkanethiol / Pt	<15° (IRAS) [03Li]				
Alkanethiol / Pd(111)	14-18° (IRAS) [03Lov]	45° (IRAS) [03Lov]			
Alkanethiol / InP(110)	34° (XANES) [99Zer]				
Alkanethiol / InP(100)	51° (angle resolved XPS) [02Yam]				
Alkanethiol / GaAs(100)	57° (IR) [92She]	45° (IR) [92She]			
1,1'-Biphenyl-4-thiol / GaAs(100)	31.5° (NEXAFS) [03Sha]				
C ₁₈ H ₃₇ MgX /	25° (XPS) [98He]				

System	Tilt angle	Twist angle	Area per molecule	Structure	Superlattice
Ge-Cl(111)					
Alkanethiol / Ge-H(111)	20° (XPS) [01Han1]				
Biphenyl-4-ol / H-Si(111)	28.7° (NEXAFS) [03Zha]				
p-Terphenyl-4-ol (TPOH) / H-Si(111)	33° (NEXAFS) [03Zha]				
(Me) ₂ (C ₁₈ H ₃₇) ₂ N ⁺ / muscovite mica	38° (NEXAFS) [99Bro]				
C ₁₈ H ₃₇ SiCl ₃ / Si(001)	20° ± 4 (XR, ellipsometry) [90Tid] 21° (GIXD) [91Tid] 10° (IR) [95All] 7° (ATR-IR) [99Val] <10° (NEXAFS, XPS) [95Bie]		20.2 Å ² [91Tid]		
Cl ₃ Si-(CH ₂) ₁₆ -CN and Cl ₃ Si-(CH ₂) ₁₆ -Br / Si/SiO ₂	21° (ATR-IR) [99Val]				
C ₁₈ H ₃₇ Si(OMe) ₃ / Cr/CrO ₂	9° (NEXAFS) [98Hil]				

Table 2. Advancing contact angles θ_a of water and hexadecane on differently substituted alkanethiol SAMs on gold (111).

Thiol	θ_a (H ₂ O) [°]	θ_a (C ₁₆ H ₃₄) [°]	Ref.
HS(CH ₂) ₂ (CF ₂) ₅ CF ₃	118	71	89Bai
HS(CH ₂) ₁₇ CH ₃	112	47	89Bai
HS(CH ₂) ₁₇ CH=CH ₂	107	39	89Bai
HS(CH ₂) ₁₉ Br	97	<5	89Bai
HS(CH ₂) ₁₁ OCOCF ₃	96	62	89Bai
HS(CH ₂) ₁₉ F	95	<5	89Bai
HS(CH ₂) ₁₉ Cl	83	<5	89Bai
HS(CH ₂) ₁₆ OCH ₃	75	41	89Bai
HS(CH ₂) ₁₀ CO ₂ CH ₃	67	28	89Bai
HS(CH ₂) ₁₁ CN	63	<5	89Bai
HS(CH ₂) ₁₀ CONH ₂	13	<5	89Bai
HS(CH ₂) ₁₅ CO ₂ H	<10	<5	89Bai
HS(CH ₂) ₁₁ OH	<10	<5	89Bai
Thiophenol	80		93Sab
4-Biphenylthiol	85		93Sab
4-Terphenylthiol	80		93Sab
HS-(C ₆ H ₄) ₂ -CH ₃	85		01Kan
HS-(C ₆ H ₄) ₂ -CF ₃	85		01Kan
HS-(C ₆ H ₄) ₂ -OH	30		01Kan
HS-(C ₆ H ₄) ₂ -F	84		01Kan
HS-(C ₆ H ₄) ₂ -Cl	90		01Kan
HS-(C ₆ H ₄) ₂ -Br	81		01Kan
HS-(C ₆ H ₄) ₂ -I	79		01Kan

Thiol	θ_a (H ₂ O) [°]	θ_a (C ₁₆ H ₃₄) [°]	Ref.
HS-(C ₆ H ₄) ₂ -CO ₂ Et	65		01Kan
HS-(C ₆ H ₄) ₂ -CHOHCH ₃	60		01Kan
HS-(C ₆ H ₄) ₂ -OEtOMe	61		01Kan
HS-(C ₆ H ₄) ₂ -NO ₂	64		01Kan
HS-(C ₆ H ₄) ₂ -N(CH ₃) ₂	66		01Kan
HS-(C ₆ H ₄) ₂ -SH	67		01Kan
HS-(C ₆ H ₄) ₂ -SCH ₃	70		01Kan
HS-(C ₆ H ₄) ₂ -COCH ₃	55		01Kan
HS-(C ₆ H ₄) ₂ -pyridine	28		01Kan

Table 3. Anchor groups for self-assembled monolayers on flat and particle substrates.

Anchor group	Substrate	Flat surfaces	Particle surfaces
RSH	Au	[87Por] [88Bai1] [88Bai2] [89Bai] [91Lai] [96Poi] [96Ulm] [98Lai] [00Sch] [00Ulm] [01Ulm] [02Eve]	[95Bru] [96Bad] [97Bad1] [97Bad2]
RSH	Ag	[91Fen] [91Lai] [91Wal] [92Lai] [96Sam] [98Hut] [99Fel] [99Scho] [00Fre] [01Kan] [01Ron]	[97Sar] [98Kan2]
RSH	Cu	[91Lai] [93Yam] [98Jen] [98Ron1] [00Sun]	[02Tzh]
RSH	Pd	[02Lov]	[99Yee3] [00Che] [00Cli] [01Zam] [02Qui]
RSH	Pt	[91Gui] [95Hin]	[98Das] [99Yee2] [01Pet] [02Zha]
RSH	Hg	[93Dem] [96Mus] [99Mus] [01Slo]	
RSH	Fe	[89Vol] [92Vol] [95Che] [95Rei] [97Noz]	[94Roz] [96Kat] [97Kat] [98Kat]
RSH	Ni	[97Mek] [98Kan1] [00Kan]	
RSH	Ir		[99Yee3]
RSH	Ge/GeH	[01Han1]	
RSH	GaAs	[92Bai] [92She]	
RSH	InP	[95Gu] [99Yam] [99Zer]	
RSH	Indium tin oxide (ITO)	[00Yan] [02Bre]	
RSH	Oxidised Au	[94Ron] [98Ron2] [98Ron3] [99Yan] [00Woo]	
RSH	χ -Fe ₂ O ₃		[96Liu] [97Kat] [98Pro]
RSSR'	Au	[83Nuz] [92Hic] [93Bie] [94Bie] [94Off] [96Beu] [96Cas] [98Che] [98Lee1] [98Nel] [99Hei] [00Gro]	[98Por] [01Sho]
RSR'	Au	[88Tro] [89Til] [93Hag] [94Zho] [98Tre] [99Zho] [00Tak]	[02She]
RSR'	Ag	[95Hei]	
RSO ₂ H	Au	[93Cha] [94Gar] [95Gar] [98Lee2]	
RSO ₂ H	Ag	[98Cao] [99Cao] [01Cao]	
RSO ₃ H	Au	[95Gar] [98Lee2]	
RSO ₃ H	Ag	[93Tar] [98Hut] [01Cao]	
RSO ₃ H	FeO _x		[99Yee1]
RSeH	Au, Ag	[92Sam] [97Dis] [98Hua] [01Han2]	
RSeSeR'	Au	[98Ban] [98Hua] [99Ban] [01Han2]	
RSeSeR'	Ag	[99Ven]	
R ₃ P	Au	[95Uvd] [98Kar]	

Anchor group	Substrate	Flat surfaces	Particle surfaces
R ₃ P	Ag	[98Kar]	
R ₃ P	Cu	[98Kar]	
R ₃ P	Rh	[98Uvd] [01Sad]	
R ₃ P=O	Graphite	[00Jia]	
RNC	Au	[92Hic] [96Hen] [99Lin] [00Hen]	[95Shi] [98Ont1] [98Ont2]
RNC	Ag	[99Han]	
RNC	Pt	[89Hic] [92Hic] [01Hor]	[99Hor]
RNC	Cr	[99Clo]	
RCOOH	Metal oxides (AgO, CuO, Al ₂ O ₃ etc.)	[82Gol] [84All] [85All1] [85All2] [93Sam] [93Tao] [96Ulm]	[95Liu] [99Kat]
RCOOH	Indium tin oxide (ITO)	[00Yan]	
RCONHOH	Metal oxides (AgO, CuO, Al ₂ O ₃ etc.)	[95Fol]	
RSiCl ₃ , RSi(OR) ₃ , RSiMe ₂ Cl	SiO ₂ , glass, Fe ₂ O ₃ , Al ₂ O ₃ , Mica, ZnSe, GeO ₂ , AuO, Si ₃ N ₄	[80Sag] [88Til] [89Was] [90Ulm] [95Moa] [96Ulm] [99Ste] [00Sch]	[96Van]
RSiCl ₃	Indium tin oxide (ITO)	[03Lus]	
RPO ₃ H ₂	ZrO ₂ , In ₂ O ₃ /SnO ₂ , CuO, AgO, Al ₂ O ₃ , Fe ₂ O ₃	[95Fol] [96Gao] [96Woo]	[99Yee1] [02Paw]
RPO ₃ H ₂	Sapphire	[01Mes]	
RPO ₃ H ₂	Ti/TiO ₂	[01Gaw]	
RPO ₃ H ₂	Ta ₂ O ₅	[00Tex]	
RPO ₃ H ₂	Indium tin oxide (ITO)	[02Bre]	
RPO ₃ H ₂	ZrO ₂		[02Yim]
(RCOO) ₂	Si/SiH	[93Lin]	
RLi	Si/SiH	[99Kim]	
RLi, RMgX	Si/SiCl	[94Che] [01Ban]	
RMgX	Ge/GeCl	[98He]	
ROH	Si/SiH	[95Cle] [00Bou] [01Bar][03Zha]	
RCHO	Si/SiH	[98Eff] [00Bou]	
RCH=CH ₂	Si/SiH	[95Lin] [98Eff] [99Bou] [01Bar]	
R ₄ N ⁺ X ⁻	Mica	[97Woo] [98Hay]	

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3.8.10.5 References for 3.8.10

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