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(71) Applicant: THE UNIVERSITY OF HOUSTON SYSTEM [US/US]; 4800 Calhoun Rd., Houston, TX 77004 (US).

(72) Inventors: LEE, T. Randall; University of Houston, Department of Chemistry, Fleming Building, Houston, TX 77204-5003 (US). **RITTIKULSITTICHAI, Supachai**; University of Houston, Department of Chemistry, Fleming Building, Houston, TX 77204-5003 (US). **FRANK, Thomas**; University of Houston, Department of Chemistry, Fleming Building, Houston, TX 77204-5003 (US). **SINGHANA, Burapol**; University of Houston, Department of Chemistry, Fleming Building, Houston, TX 77204-5003 (US).

(74) Agent: STROZIER, Robert W.; P.O. Box 429, Bellaire, TX 77402-0429 (US).

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[Continued on next page]

(54) Title: STABLE HOMOGENEOUSLY MIXED NANOSCALE COATINGS DERIVED FROM UNIQUE MULTI-FUNCTIONAL AND MULTIDENTATE AROMATIC ADSORBATES

(57) Abstract: Novel tridentate-, bidentate-, and monodentate-based aromatic adsorbates including self-assembled monolayers (SAMs), especially, mixed multi-component SAMs, where the adsorbates comprise an aromatic ring including one head group or a plurality of dentate head groups and one tunable tail group or a plurality of tail groups and methods for making the same, and methods for using same, their use in the preparation of homogeneously mixed multi-component self-assembled monolayers (SAMs). The adsorbants and SAMs derived therefrom are ideally suited for biosensing, biosensing diagnostics, biological interfacial mimics, surface protections for nanoparticles, inert coatings for artificial implants, and corrosion-resistant coatings for microelectronics components.

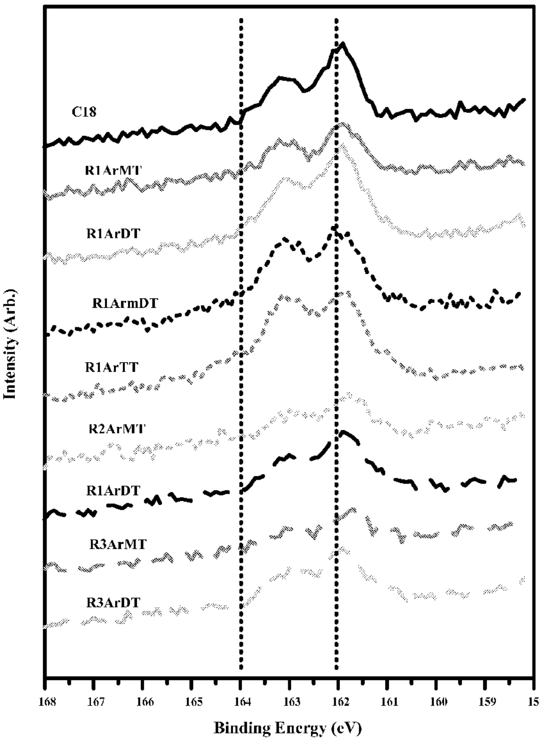

FIG. 1

WO 2013/134520 A1

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PCT SPECIFICATION

TITLE: **STABLE HOMOGENEOUSLY MIXED NANOSCALE COATINGS DERIVED FROM UNIQUE MULTI-FUNCTIONAL AND MULTIDENTATE AROMATIC ADSORBATES**

INVENTOR: **T. Randall LEE (Houston, TX), Supachai RITTIKULSITTICHAI (Houston, TX), Thomas FRANK (Houston, TX), and Burapol SINGHANA (Houston, TX)**

ASSIGNEE: **THE UNIVERSITY OF HOUSTON SYSTEM**

RELATED APPLICATIONS

[0001] This application claims the benefit to and priority to United States Provisional Application Serial Number 61/607,710 filed 7 March 2012 (03/07/2012).

GOVERNMENTAL SPONSORSHIP

[0002] Not Applicable.

REFERENCE TO A SEQUENTIAL LISTING

[0003] Not Applicable.

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0004] Embodiments of the present invention relate to the compositions of new tridentate-, bidentate-, and monodentate-based aromatic adsorbates, methods for making the same, and methods for their use in the preparation of self-assembled monolayer and especially homogeneously mixed multi-component self-assembled monolayers (SAMs). Embodiments of the compositions exhibit homogenous lateral chain distributions, no phase separation or islanding across the surfaces, and enhanced stability as compared to standard monodentate adsorbates. Embodiments of the compositions of this invention are well suited for such applications as, without limitation, biosensing, biosensing diagnostics, biological interfacial mimics, surface protections for nanoparticles, inert coatings for artificial implants, and corrosion-resistant coatings for microelectronics components.

2. Description of the Related Art

[0005] Ultrathin organic coatings have become a promising strategy for modern material science, especially, a method of surface functionalization, because they offer a wide range of chemical functionalities, which can be adjusted and tailored via organic synthetic transformations to make chemical compositions having specific tail groups to fabricate custom-designed SAMs for specific applications. The successful use of these modified surface materials for most of practical applications (*i.e.*, nanofabrication,[1] microelectronic devices,[2,3] and mechanical interfacial applications involving friction,[4,5] corrosion,[6,7] lubrication, and adhesion[8,9]) critically relies on their stabilities. Furthermore, several applications (*e.g.*, platforms for chemical and biological sensors,[10,11] artificial implants[12,13]) require complex mixed surface functionalities, where the lateral distribution of chemical functionalities are homogeneous across surfaces and can be precisely controlled at the nano-scales. Numerous approaches have been utilized for the preparation of mixed SAM coatings, including the use of unsymmetrical dialkyl sulfides or dialkyl sulfides,[14,15] the use of two or more different adsorbates[16], and the use of ligand-exchange methods.[17] However, SAM coatings derived by these strategies are critically limited due to the difficulty in controlling the distribution and the ratios of the two (or more) adsorbates. Moreover, several studies have found that these types of SAMs are unstable and suffer from phase separation (*i.e.*, the formation of segregated domains or "islands" of each adsorbate). While other fabrication techniques such as microcontact printing and lithographic methods have been developed to pattern multicomponent SAMs on surfaces,[1] most of these techniques are costly and suffer from degradation due to molecular desorption and/or diffusion.

[0006] Thus, there is a need in the art for compositions capable of producing stable mixed SAMs, for methods of preparing the compositions, SAM modified substrates, and apparatus incorporating the SAM modified substrates.

SUMMARY OF THE INVENTION

[0007] As an improvement over disadvantages of aforementioned strategies, embodiments of the present invention provide novel and convenient methods for preparing SAMs and especially homogeneously mixed multi-component SAMs via the adsorption of new tridentate-, bidentate-, and monodentate-based aromatic adsorbates non-symmetrical spiroalkanedithiols onto appropriate surfaces including metal surfaces.[18,19] Embodiments of the present invention also provide that mixed SAMs derived from this class of bidentate adsorbate exhibit homogenous lateral chain distributions, no phase separation or islanding across SAM modified surfaces, and enhanced stability as compared to standard monodentate adsorbates. Embodiments of the present invention also provide absorbates having three different tail groups.

[0008] Embodiments of the present invention provide mono-, bi-, and tri-dentate absorbates for the preparation of self-assembled monolayers (SAMs), especially, mixed multi-component SAMs, where the adsorbates comprise an aromatic ring including one head group or a plurality of dentate head groups and one tunable tail group or a plurality of tail groups designated, Z^1, Z^2, and Z^3 groups. Embodiments for these adsorbates comprise compounds of the general formula (I):

$$\mathbf{Z^1,Z^2,Z^3\text{–}A(SH)_k(RSH)_l(CH_{m1}(SH)_{m2})_n} \qquad \text{(I)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) **Z^1**, **Z^2**, and **Z^3** groups are the same or different and comprise a hydrogen atom, a carbyl group **R^{a1}**, halogenated carbyl group **R^{a2}**, a fluorinated carbyl group **R^{a3}**, a per-fluorinated carbyl group **R^{a4}**, an alkoxy group **OR^b** group, an amine group **NR^cR^d**, an amido group **$C(O)NR^eR^f$**, an amido group **$NR^xC(O)R^y$**, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the **Z^1**, **Z^2**, or **Z^3** groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the **R^{a1}** and the **$R^{c,e,y}$** groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, **NR^g** groups, **$C(O)NR^hR^i$** groups, or **$NR^wC(O)R^z$** groups, (5) the **$R^{a2\text{-}a4}$** may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the **$R^{d,f,x}$** groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, (7) **$R^{g,h,i,w,z}$** are linear or branched carbyl groups having between 1 and 10 carbon atoms, (8) **k**, **l**, **m1**, **m2** and **n** are integers, (9) **k** has a value between 1 and 3, when **l** and **n** have a value of 0, (10) **l** has a value between 1 and 3, when **k** and **n** have a value of 0, (11) **n** has a value of 1, when **k** and **l** have a value of 0, and (12) **m1** + **m2** is equal to 3. In certain embodiments, at least two of **Z^1**, **Z^2**, and **Z^3** groups are not hydrogen atoms. In other embodiments, all of the **Z^1**, **Z^2**, and **Z^3** groups are not hydrogen atoms.

[0009] Embodiments of the present invention provide mono-, bi- and tri-dentate absorbates for the preparation of self-assembled monolayers (SAMs), especially, mixed multi-component SAMs, where the adsorbates comprise compounds of the general formula (II):

$$\mathbf{Z^1,Z^2,Z^3\text{-}ACH_{m1}(SH)_{m2}} \qquad \text{(II)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) **Z^1**, **Z^2**, and **Z^3** groups are the same or different and comprise a hydrogen atom, a carbyl group **R^{a1}**, halogenated carbyl group **R^{a2}**, a fluorinated carbyl group **R^{a3}**, a per-fluorinated carbyl group **R^{a4}**, an alkoxy group **OR^b** group, an amine group **NR^cR^d**, an amido group **$C(O)NR^eR^f$**, an amido group **$NR^xC(O)R^y$**, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the **Z^1**, **Z^2**, or **Z^3** groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the **R^{a1}** and the **$R^{c,e,y}$** groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, **NR^g** groups, **$C(O)NR^hR^i$** groups, or **$NR^wC(O)R^z$** groups, (5) the **$R^{a2\text{-}a4}$** may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the $\mathbf{R}^{d,f,x}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, (7) $\mathbf{R}^{g,h,i,w,z}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms, (8) **m1** and **m2** are integers, and (9) **m1** + **m2** is equal to 3. In certain embodiments, at least two of $\mathbf{Z}^1$, $\mathbf{Z}^2$, and $\mathbf{Z}^3$ groups are not hydrogen atoms. In other embodiments, all of the $\mathbf{Z}^1$, $\mathbf{Z}^2$, and $\mathbf{Z}^3$ groups are not hydrogen atoms.

[0010] Embodiments of the present invention provide mono-, bi- and tri-dentate absorbates for the preparation of self-assembled monolayers (SAMs), especially, mixed multi-component SAMs, where the adsorbates comprise compounds of the general formula (III):

$$\mathbf{Z^1,Z^2,Z^3\text{-}A\text{-}m\text{-}(RSH)_2} \qquad \text{(III)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) $\mathbf{Z}^1$, $\mathbf{Z}^2$, and $\mathbf{Z}^3$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R}^{a1}$, halogenated carbyl group $\mathbf{R}^{a2}$, a fluorinated carbyl group $\mathbf{R}^{a3}$, a per-fluorinated carbyl group $\mathbf{R}^{a4}$, an alkoxy group $\mathbf{OR}^b$ group, an amine group $\mathbf{NR}^c\mathbf{R}^d$, an amido group $\mathbf{C(O)NR}^e\mathbf{R}^f$, an amido group $\mathbf{NR}^x\mathbf{C(O)R}^y$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z}^1$, $\mathbf{Z}^2$, or $\mathbf{Z}^3$ groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the $\mathbf{R}^{a1}$ and the $\mathbf{R}^{c,e,y}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR}^g$ groups, $\mathbf{C(O)NR}^h\mathbf{R}^i$ groups, or $\mathbf{NR}^w\mathbf{C(O)R}^z$ groups, (5) the $\mathbf{R}^{a2\text{-}a4}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the $\mathbf{R}^{d,f,x}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (7) $\mathbf{R}^{g,h,i,w,z}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms. In certain embodiments, at least two of $\mathbf{Z}^1$, $\mathbf{Z}^2$, and $\mathbf{Z}^3$ groups are not hydrogen atoms. In other embodiments, all of the $\mathbf{Z}^1$, $\mathbf{Z}^2$, and $\mathbf{Z}^3$ groups are not hydrogen atoms.

[0011] Embodiments of the present invention provide mono-, bi- and tri-dentate absorbates for the preparation of self-assembled monolayers (SAMs), especially, mixed multi-component SAMs, where the adsorbates comprise compounds of the general formula (IV):

$$\mathbf{Z^1,Z^2,Z^3\text{-}Py\text{-}m\text{-}(RSH)_2} \qquad \text{(IV)}$$

where: (1) **Py** is pyridine, (2) **-m-** means the two **RSH** groups meta to each other, (3) $\mathbf{Z}^1$, $\mathbf{Z}^2$, and $\mathbf{Z}^3$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R}^{a1}$, halogenated carbyl group $\mathbf{R}^{a2}$, a fluorinated carbyl group $\mathbf{R}^{a3}$, a per-fluorinated carbyl group $\mathbf{R}^{a4}$, an alkoxy group $\mathbf{OR}^b$ group, an amine group $\mathbf{NR}^c\mathbf{R}^d$, an amido group $\mathbf{C(O)NR}^e\mathbf{R}^f$, an amido group $\mathbf{NR}^x\mathbf{C(O)R}^y$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups is not hydrogen, (4) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (5) the $\mathbf{R^{a1}}$ and the $\mathbf{R^{c,e,y}}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR^g}$ groups, $\mathbf{C(O)NR^hR^i}$ groups, or $\mathbf{NR^wC(O)R^z}$ groups, (6) the $\mathbf{R^{a2\text{-}a4}}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (7) the $\mathbf{R^{d,f,x}}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (8) $\mathbf{R^{g,h,i,w,z}}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms. In certain embodiments, at least two of the $\mathbf{Z^1}$, $\mathbf{Z^2}$ and $\mathbf{Z^3}$ groups are not a hydrogen atom. In other embodiments, all of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are not a hydrogen atom.

[0012] Embodiments of the present invention provide mono-, bi- and tri-dentate absorbates for the preparation of self-assembled monolayers (SAMs), especially, mixed multi-component SAMs, where the adsorbates comprise compounds of the general formula (V):

$$\mathbf{Z^1,Z^2\text{-}Cp\text{-}m\text{-}(RSH)_2} \qquad \text{(V)}$$

where: (1) **Cp** is 5-member aromatic ring, where one of the carbon atoms of the **Cp** ring may be replaced by an oxygen atom, a nitrogen atom, or a sulfur atom, (2) **-m-** means that the two **RSH** groups are meta to each other or occupy the 2 and 5 positions of the five membered **Cp** ring, (3) $\mathbf{Z^1}$ and $\mathbf{Z^2}$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R^{a1}}$, halogenated carbyl group $\mathbf{R^{a2}}$, a fluorinated carbyl group $\mathbf{R^{a3}}$, a per-fluorinated carbyl group $\mathbf{R^{a4}}$, an alkoxy group $\mathbf{OR^b}$ group, an amine group $\mathbf{NR^cR^d}$, an amido group $\mathbf{C(O)NR^eR^f}$, an amido group $\mathbf{NR^xC(O)R^y}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z^1}$ and $\mathbf{Z^2}$ groups is not a hydrogen atom, (4) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (5) the $\mathbf{R^{a1}}$ and the $\mathbf{R^{c,e,y}}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR^g}$ groups, $\mathbf{C(O)NR^hR^i}$ groups, or $\mathbf{NR^wC(O)R^z}$ groups, (6) the $\mathbf{R^{a2\text{-}a4}}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (7) the $\mathbf{R^{d,f,x}}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (8) $\mathbf{R^{g,h,i,w,z}}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms. In certain embodiments, at least two of the $\mathbf{Z^1}$, $\mathbf{Z^2}$ and $\mathbf{Z^3}$ groups are not a hydrogen atom. In other embodiments, all of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are not a hydrogen atom.

[0013] Embodiments of the present invention provide SAMs comprising two or more compounds set forth above.

[0014] Embodiments of the present invention provide substrates having SAMs comprising two or more compounds set forth above.

[0015] Embodiments of the present invention provide methods for preparing the mono-, bi- and tridentate absorbates of this invention.

[0016] Embodiments of the present invention provide methods for preparing SAMs comprising two or more compounds set forth above.

[0017] Embodiments of the present invention provide methods for preparing substrates including SAMs comprising two or more compounds set forth above.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] The invention can be better understood with reference to the following detailed description together with the appended illustrative drawings in which like elements are numbered the same:

[0019] **Figure 1** depicts XPS spectra showing the S 2p region for monolayer films derived from **C18** thiol absorbate and new classes of multidentate aromatic thiols.

[0020] **Figure 2** depicts PM-IRRAS spectra showing the C-H stretching region for monolayer films derived from **C18** thiol absorbate and new classes of multidentate aromatic adsorbates.

[0021] **Figure 3** depicts Desorption profiles of SAMs derived from **C18** thiol absorbate and new classes of multidentate aromatic adsorbates.

DETAILED DESCRIPTION OF THE INVENTION

[0022] Embodiments of the present invention relates to compositions of new tridentate-, bidentate-, and monodentate-based aromatic adsorbates, methods for making the same, and methods for their use in the preparation of homogeneously mixed multi-component self-assembled monolayers (SAMs). Such systems exhibit homogenous lateral chain distributions, no phase separation (or islanding) across substrate surfaces, and enhanced stability as compared to standard monodentate adsorbates. Applications of such systems include, without limitation, biosensing, biosensing diagnostics, biological interfacial mimics, surface protections for nanoparticles, inert coatings for artificial implants, and corrosion-resistant coatings for microelectronics components.

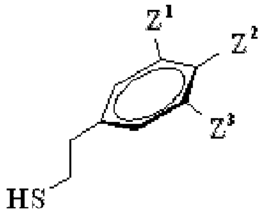
[0023] Generally speaking, the present invention meets fundamental requirements for the use of self-assembled monolayers in research and commercial applications: (1) long-term stability of such coatings under ambient temperatures, elevated temperatures, physiological conditions, and/or sterilization conditions, and (2) facile tunability in the tail group composition and thus the surface composition, allowing the specific designs of the surfaces for certain applications.

[0024] Embodiments of the present invention provide mono-, bi-, and tri-dentate absorbates for the preparation of self-assembled monolayers (SAMs), especially, mixed multi-component SAMs, where the adsorbates comprise an aromatic ring including one head group or a plurality of dentate head groups and one tunable tail group or a plurality of tail groups designated, Z^1, Z^2, and Z^3 groups. Embodiments for these adsorbates comprise compounds of the general formula (I):

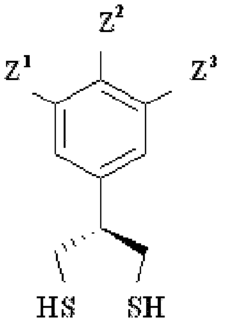
$$\mathbf{Z^1,Z^2,Z^3\text{-}A(SH)_k(RSH)_l(CH_{m1}(SH)_{m2})_n} \qquad \text{(I)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) **Z^1**, **Z^2**, and **Z^3** groups are the same or different and comprise a hydrogen atom, a carbyl group **R^{a1}**, halogenated carbyl group **R^{a2}**, a fluorinated carbyl group **R^{a3}**, a per-fluorinated carbyl group **R^{a4}**, an alkoxy group **OR^b** group, an amine group **NR^cR^d**, an amido group **$C(O)NR^eR^f$**, an amido group **$NR^xC(O)R^y$**, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the **Z^1**, **Z^2**, or **Z^3** groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the **R^{a1}** and the **$R^{c,e,y}$** groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, **NR^g** groups, **$C(O)NR^hR^i$** groups, or **$NR^wC(O)R^z$** groups, (5) the **$R^{a2\text{-}a4}$** may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the **$R^{d,f,x}$** groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, (7) **$R^{g,h,i,w,z}$** are linear or branched carbyl groups having between 1 and 10 carbon atoms, (8) **k**, **l**, **m1**, **m2** and **n** are integers, (9) **k** has a value between 1 and 3, when **l** and **n** have a value of 0, (10) **l** has a value between 1 and 3, when **k** and **n** have a value of 0, (11) **n** has a value of 1, when **k** and **l** have a value of 0, and (12) **m1** + **m2** is equal to 3. In certain embodiments, at least two of **Z^1**, **Z^2**, and **Z^3** groups are not hydrogen atoms. In other embodiments, all of the **Z^1**, **Z^2**, and **Z^3** groups are not hydrogen atoms.

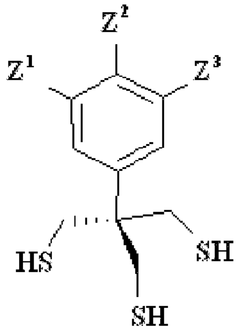
[0025] The prototypical structures of the new multidentate-based aromatic adsorbates are shown below:



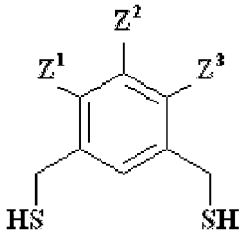
Mono-$CZ^1Z^2Z^3$



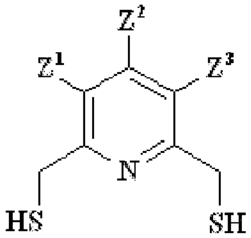
Bis-$CZ^1Z^2Z^3$



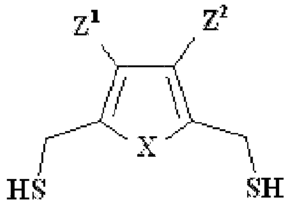
Tris-$CZ^1Z^2Z^3$



mBis-$CZ^1Z^2Z^3$



mBis-$PyZ^1Z^2Z^3$



mBis-CpZ^1Z^2

These unique adsorbates comprise an aromatic ring including one or multidentate head groups and one or tunable tail groups designated $\mathbf{Z^1}$, $\mathbf{Z^2}$, or $\mathbf{Z^3}$ groups.

[0026] Embodiments of the present invention provide mono-, bi- and tri-dentate absorbates for the preparation of self-assembled monolayers (SAMs), especially, mixed multi-component SAMs, where the adsorbates comprise compounds of the general formula (II):

$$\mathbf{Z^1,Z^2,Z^3\text{-}ACH_{m1}(SH)_{m2}} \qquad \text{(II)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R^{a1}}$, halogenated carbyl group $\mathbf{R^{a2}}$, a fluorinated carbyl group $\mathbf{R^{a3}}$, a per-fluorinated carbyl group $\mathbf{R^{a4}}$, an alkoxy group $\mathbf{OR^b}$ group, an amine group $\mathbf{NR^cR^d}$, an amido group $\mathbf{C(O)NR^eR^f}$, an amido group $\mathbf{NR^xC(O)R^y}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, or $\mathbf{Z^3}$ groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the $\mathbf{R^{a1}}$ and the $\mathbf{R^{c,e,y}}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, **NR^g** groups, **C(O)NR^{h}R^i** groups, or **NR^{w}C(O)R^z** groups, (5) the **R^{a2-a4}** may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the **R^{d,f,x}** groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, (7) **R^{g,h,i,w,z}** are linear or branched carbyl groups having between 1 and 10 carbon atoms, (8) **m1** and **m2** are integers, and (9) **m1** + **m2** is equal to 3. In certain embodiments, at least two of **Z^1**, **Z^2**, and **Z^3** groups are not hydrogen atoms. In other embodiments, all of the **Z^1**, **Z^2**, and **Z^3** groups are not hydrogen atoms.

[0027] Embodiments of the present invention provide mono-, bi- and tri-dentate absorbates for the preparation of self-assembled monolayers (SAMs), especially, mixed multi-component SAMs, where the adsorbates comprise compounds of the general formula (III):

$$\mathbf{Z^1,Z^2,Z^3\text{-}A\text{-}m\text{-}(RSH)_2} \qquad \text{(III)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) **Z^1**, **Z^2**, and **Z^3** groups are the same or different and comprise a hydrogen atom, a carbyl group **R^{a1}**, halogenated carbyl group **R^{a2}**, a fluorinated carbyl group **R^{a3}**, a per-fluorinated carbyl group **R^{a4}**, an alkoxy group **OR^b** group, an amine group **NR^{c}R^d**, an amido group **C(O)NR^{e}R^f**, an amido group **NR^{x}C(O)R^y**, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the **Z^1**, **Z^2**, or **Z^3** groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the **R^{a1}** and the **R^{c,e,y}** groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, **NR^g** groups, **C(O)NR^{h}R^i** groups, or **NR^{w}C(O)R^z** groups, (5) the **R^{a2-a4}** may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the **R^{d,f,x}** groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (7) **R^{g,h,i,w,z}** are linear or branched carbyl groups having between 1 and 10 carbon atoms. In certain embodiments, at least two of **Z^1**, **Z^2**, and **Z^3** groups are not hydrogen atoms. In other embodiments, all of the **Z^1**, **Z^2**, and **Z^3** groups are not hydrogen atoms.

[0028] Embodiments of the present invention provide mono-, bi- and tri-dentate absorbates for the preparation of self-assembled monolayers (SAMs), especially, mixed multi-component SAMs, where the adsorbates comprise compounds of the general formula (IV):

$$\mathbf{Z^1,Z^2,Z^3\text{-}Py\text{-}m\text{-}(RSH)_2} \qquad \text{(IV)}$$

where: (1) **Py** is pyridine, (2) **-m-** means the two **RSH** groups meta to each other, (3) **Z^1**, **Z^2**, and **Z^3** groups are the same or different and comprise a hydrogen atom, a carbyl group **R^{a1}**, halogenated carbyl group $\mathbf{R^{a2}}$, a fluorinated carbyl group $\mathbf{R^{a3}}$, a per-fluorinated carbyl group $\mathbf{R^{a4}}$, an alkoxy group $\mathbf{OR^{b}}$ group, an amine group $\mathbf{NR^{c}R^{d}}$, an amido group $\mathbf{C(O)NR^{e}R^{f}}$, an amido group $\mathbf{NR^{x}C(O)R^{y}}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups is not hydrogen, (4) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (5) the $\mathbf{R^{a1}}$ and the $\mathbf{R^{c,e,y}}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR^{g}}$ groups, $\mathbf{C(O)NR^{h}R^{i}}$ groups, or $\mathbf{NR^{w}C(O)R^{z}}$ groups, (6) the $\mathbf{R^{a2\text{-}a4}}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (7) the $\mathbf{R^{d,f,x}}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (8) $\mathbf{R^{g,h,i,w,z}}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms. In certain embodiments, at least two of the $\mathbf{Z^1}$, $\mathbf{Z^2}$ and $\mathbf{Z^3}$ groups are not a hydrogen atom. In other embodiments, all of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are not a hydrogen atom.

[0029] Embodiments of the present invention provide mono-, bi- and tri-dentate absorbates for the preparation of self-assembled monolayers (SAMs), especially, mixed multi-component SAMs, where the adsorbates comprise compounds of the general formula (V):

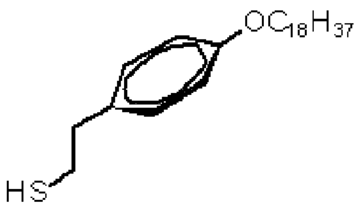
$$\mathbf{Z^1,Z^2\text{-}Cp\text{-}m\text{-}(RSH)_2} \tag{V}$$

where: (1) **Cp** is 5-member aromatic ring, where one of the carbon atoms of the **Cp** ring may be replaced by an oxygen atom, a nitrogen atom, or a sulfur atom, (2) **-m-** means that the two **RSH** groups are meta to each other or occupy the 2 and 5 positions of the five membered **Cp** ring, (3) $\mathbf{Z^1}$ and $\mathbf{Z^2}$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R^{a1}}$, halogenated carbyl group $\mathbf{R^{a2}}$, a fluorinated carbyl group $\mathbf{R^{a3}}$, a per-fluorinated carbyl group $\mathbf{R^{a4}}$, an alkoxy group $\mathbf{OR^{b}}$ group, an amine group $\mathbf{NR^{c}R^{d}}$, an amido group $\mathbf{C(O)NR^{e}R^{f}}$, an amido group $\mathbf{NR^{x}C(O)R^{y}}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z^1}$ and $\mathbf{Z^2}$ groups is not a hydrogen atom, (4) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (5) the $\mathbf{R^{a1}}$ and the $\mathbf{R^{c,e,y}}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR^{g}}$ groups, $\mathbf{C(O)NR^{h}R^{i}}$ groups, or $\mathbf{NR^{w}C(O)R^{z}}$ groups, (6) the $\mathbf{R^{a2\text{-}a4}}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (7) the $\mathbf{R^{d,f,x}}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (8) $\mathbf{R^{g,h,i,w,z}}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms. In certain embodiments, at least two of the **Z**^{1}, **Z**^{2} and **Z**^{3} groups are not a hydrogen atom. In other embodiments, all of the **Z**^{1}, **Z**^{2}, and **Z**^{3} groups are not a hydrogen atom.

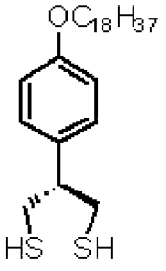
[0030] Embodiments of this invention systematic studies self-assembled monolayers (SAMs) derived from a series of four different new adsorbates designated **Series I**, **Series II**, **Series III**, and **Series IV**, as described in the subsequent paragraphs. Such systematic study helps establish the fundamental guidelines for the molecular designs and structure-property relationships of the organic monolayer films based on these aromatic chelating adsorbates. Of particular interest here are investigations that focus on the differences in the commensurability between the chelating head groups and the numbers of hydrocarbon chain tail groups, structural conformations, molecular packing densities, chain packing densities, and thermal stabilities for these monolayers. Such investigations lead to a better understanding of the factors that govern structurally complex monolayer interfaces and allow us to generate and study model interfaces that mimic the complexity found in the nature (*e.g.*, cell surface) and in advanced applied materials.

Series I (R1ArMT, R1ArDT, and R1ArTT)

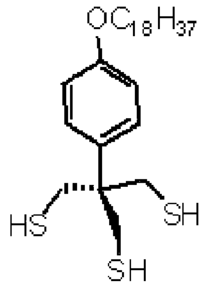
[0031] This series includes adsorbates of general formula **R1ArMT**, **R1ArDT**, and **R1ArTT**, where **R1** = alkyl or alkoxy chain (*e.g.*, $-C_nH_{2n+1}$ or $-OC_nH_{2n+1}$), **Ar** = aromatic moiety (*e.g.*, $-C_6H_4$), **MT** = monothiol (*e.g.*, $-CH_2CH_2SH$), **DT** = dithiol (*e.g.*, $-CH(CH_2SH)_2$), and **TT** = trithiol (*e.g.*, $-C(CH_2SH)_3$). The aromatic-based adsorbate molecules in this series are comprised of tri, di, and monothiolate head groups connecting to the intervening benzene ring with the single chain of hydrocarbon tail group placed at the opposite position with respect to the head group, as shown below:



R1ArMT



R1ArDT



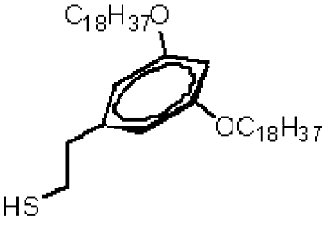
R1ArTT

In this series, the present invention teaches the influence of the multidentate head groups on the structure-property relationships, especially, thermal and chemical stability.

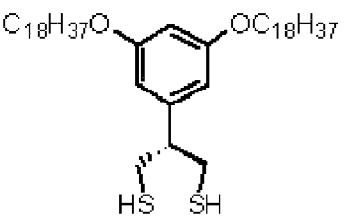
Series II (R^{2}ArMT, R^{2}ArDT, and R^{2}ArTT)

[0032] This series includes adsorbates of general formula **R^{2}ArMT**, **R^{2}ArDT**, and **R^{2}ArTT**, where

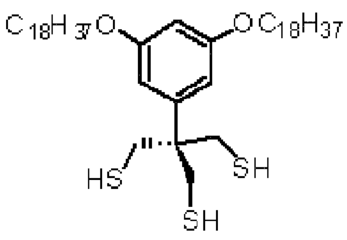
R2 = two alkyl or alkoxy chains (*e.g.*, $–C_nH_{2n+1}$ or $–OC_nH_{2n+1}$) at the 3,5-positions of the aromatic ring, **Ar** = aromatic moiety (*e.g.*, $–C_6H_3$), **MT** = monothiol (*e.g.*, $–CH_2CH_2SH$), **DT** = dithiol (*e.g.*, $–CH(CH_2SH)_2$), and **TT** = trithiol (*e.g.*, $–C(CH_2SH)_3$). The molecular structures of these adsorbates are shown below:



R2ArMT



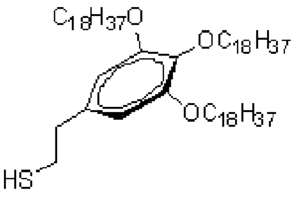
R2ArDT



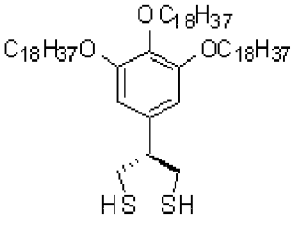
R2ArTT

Series III (R3ArMT, R3ArDT, and R3ArTT)

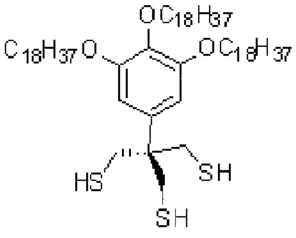
[0033] This series includes adsorbates of general formula **R3ArMT**, **R3ArDT**, and **R3ArTT**, where **R3** = three alkyl or alkoxy chains (*e.g.*, $–C_nH_{2n+1}$ or $–OC_nH_{2n+1}$) at the 3,4,5-positions of the aromatic ring, **Ar** = aromatic moiety (*e.g.*, $–C_6H_3$), **MT** = monothiol (*e.g.*, $–CH_2CH_2SH$), **DT** = dithiol (*e.g.*, $–CH(CH_2SH)_2$), and **TT** = trithiol (*e.g.*, $–C(CH_2SH)_3$). The molecular structures of these adsorbates are shown below:



R3ArMT



R3ArDT

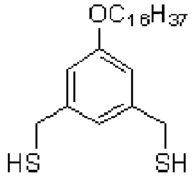


R3ArTT

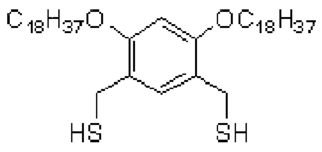
[0034] The rationale for such designs in **Series II** and **III** is that an increased number of the tail groups can increase chain assembled interactions for SAMs derived from bi- and tridentate adsorbates, which should enhance the chain packing, which in turn should enhance film stability.

Series IV (R1ArmDT, R2ArmDT, R3ArmDT, and R2CpDT)

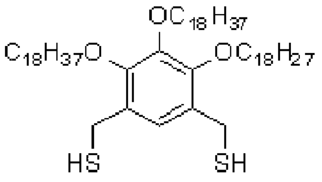
[0035] This series includes adsorbates of general formula **R1ArmDT**, **R2ArmDT**, **R3ArmDT**, and **R2CpDT**, where **R1**, **R2**, and **R3** = one, two, and three alkyl or alkoxy chains (*e.g.*, $–C_nH_{2n+1}$ or $–OC_nH_{2n+1}$) at the 5-, 4,6-, and 4,5,6-positions of the aromatic ring, respectively, **Ar** = aromatic moiety (*e.g.*, $–C_6H_3$, $–C_6H_2$, $–C_6H_1$, and pyridine analogs), **Cp** = five-membered ring analogs (*e.g.*, cyclopentadiene, pyrrole, furan, or thiophene), and **mDT** = meta-dithiol (*e.g.*, $–CH(CH_2SH)_2$). In this series, the present invention teaches the influence of the intramolecular S–S distances on the structure-property relationships, particularly the film stability. The meta-dithiol architecture for these adsorbates with tail groups incorporated at the 5-, 4,6-, and 4,5,6-position on the aromatic ring is shown below:



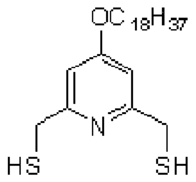
R1ArmDT



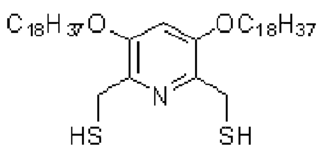
R2ArmDT



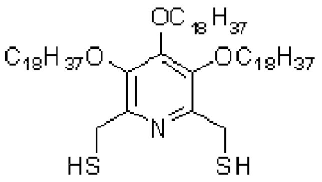
R3ArmDT



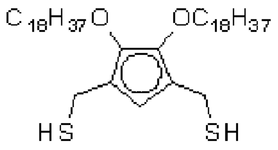
R1ArmDT



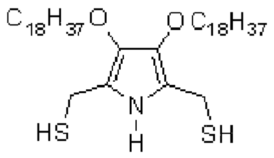
R2ArmDT



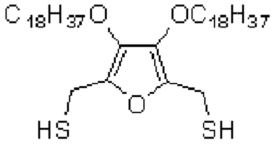
R3ArmDT



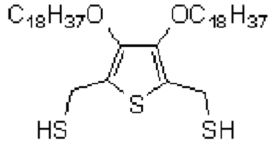
R2CCpDT



R2NCpDT



R2OCpDT



R2SCpDT

The rationale for this design is that the thiol groups are positioned in a manner that inhibits or excludes the formation of intramolecular cyclic disulfides, which should lead to films with enhanced stability by inhibiting or eliminating a key desorption pathway.[20,21] A comparison of the characteristics and thermal stabilities of films derived from **R1ArDT** and **R1ArmDT** supports this hypothesis.

[0036] The evaluation of the quality of monolayer films on metal substrates is determined by measuring the thicknesses of the resultant films using ellipsometry.[22] To understand the relationship between film thicknesses and molecular orientations as well as conformational orders of the SAMs, it is useful to compare the ellipsometric thicknesses of the monolayers with the theoretical thicknesses estimated from the models,[23] as shown in **Table 1**.

TABLE 1
Calculated Thicknesses and Measured Thicknesses for SAMs Generated from C18 and New Classes of Multidentate Aromatic Thiols

Adsorbate	Calculated Thickness (Å)	Measured Thickness (Å)*
C18	22	22
R1ArMT	28	28
R1ArDT	31	19
R1ArmDT	29	18
R1ArTT	31	18
R2ArMT	28	29
R2ArDT	30	23
R3ArMT	28	29
R3ArDT	30-31	29

*The ellipsometric thicknesses were reproducible within ± 2 Å

[0037] Embodiments of the present invention disclose that the ellipsometric thickness of SAMs derived from single-tailed adsorbates decreases with an increase of the numbers of chelating head groups, going from mono, di, and tridentate thiols. This is clearly observed in **Series I** (with adsorbates **R1ArMT**, **R1ArDT**, and **R1ArTT**). These results are consistent with a change in the sulfur-to-chain ratios of the adsorbates, which is 1:1 for **R1ArMT**, 2:1 for **R1ArDT** and 3:1 for **R1ArTT**, namely, a size mismatch between head groups and the single chain tail group. The creation of void space between individual molecules due to the incommensurability between the relatively larger size of the multidentate head groups and the single hydrocarbon chained tail group results in the weak intermolecular interactions,[24] for example, π–π stacking interactions and inter-chain interactions. Consequently, these cause the deformation and tilt of the molecular chains. With the comparison of the ellipsometric thicknesses to the theoretical values, we therefore quantitatively conclude that the degree of chain tilt of these monolayers increases as following: **R1ArTT** > **R1ArDT** > **R1ArMT**, while the trends in the chain conformational order exhibits the reverse trend from the relative chain tilt.

[0038] Other embodiments of the present invention disclose that the ellipsometric thickness of SAMs increase with increasing the numbers of branched chains, namely chain-to-sulfur ratios. This is observed in the comparisons of monolayers derived from multi-tailed adsorbates (**R3ArMT**, **R2ArMT**, **R3ArDT**, and **R2ArDT**) with those derived from single-tailed adsorbates (**R1ArMT** and **R1ArDT**). For example, the thickness values of SAMs generated from mono and bidentate adsorbates having one, two, and three tail groups increases as follows: **R3ArMT**, **R2ArMT** > **R1ArMT**, and **R3ArDT** > **R2ArDT** > **R1ArDT**, respectively. The increase of the chain-to-sulfur ratios diminishes the void volume above the phenyl ring, which therefore increases the chain packing density and the chain-chain interactions. Comparison of the estimated thicknesses with the measured thicknesses (see **Table 1**) reveals good agreement for the SAM derived from **R1ArMT**, but a slight underestimation for the SAMs derived from **R2ArMT** and **R3ArMT**. These results can be interpreted to indicate that the molecules of the **R1ArMT** SAMs tilt approximately 30° from the surface normal with the chains possessing a largely trans zig-zag conformation. On the other hand, the underestimated thicknesses for the **R2ArMT** and **R3ArMT** SAMs can be interpreted to indicate that the molecules actually tilt less than 30° and/or that the molecules pack more densely on the surface those in normal SAMs. In addition, the significantly lower measured thickness values of **R1ArDT** and **R2ArDT** SAMs as compared to those obtained from the molecular models can be rationalized as a consequence of the high degree of chain tilt and chain deformation due to the less chain assembled interactions.[24] In contrast, the ellipsometric thickness of the **R3ArDT** SAM is close to that obtained from the model, which suggests that the long alkoxy chains in **R3ArDT** monolayer are likely tilted in less degree with respects to the surface normal as compared to that in **R2ArDT** and **R3ArDT** SAMs. As whole, the results reflect that the chain-assembled interactions in the **R3ArDT** SAM is higher than those in the **R1ArDT** and **R2ArDT** SAMs. Based on the ellipsometric thickness data, the relative chain tilt of the SAMs generated from these new adsorbates can be qualitatively estimated as follows: **R1ArDT** > **R2ArDT** > **R3ArDT**, while the trends in the chain conformational order exhibits the reverse trend from the relative chain tilt.

[0039] Other embodiments of the present invention disclose that the slight variation in the S····S distance for the different designs of dithiolate head groups does not significantly influence film thicknesses. This is observed in the comparison of monolayers derived from **R1ArDT** and **R1ArmDT**. The molecular lengths determined from the models of **R1ArDT** and **R1ArmDT** exhibit in the same extent with 2Å difference. Therefore, the ellipsometric thickness values for both SAMs could be qualitatively compared to discern their structural formation (*i.e.*, chain tilt and molecular packing density). Considering the two different designs of the dithiolate head groups for these two adsorbates, **R1ArmDT** has a longer intramolecular S····S distance than **R1ArDT**. Accordingly, **R1ArmDT** would occupy a larger surface area and create a larger space between the alkyl chains above the aromatic ring than **R1ArDT**. To optimize the inter-chain interactions, the long hydrocarbon chains in the **R1ArmDT** monolayer would be more tilted than those in the **R1ArDT** monolayer. The ellipsometric thickness of the **R1ArmDT** monolayer would therefore display a noticeably lower value when compared to that of the **R1ArDT** monolayer. In fact, both monolayers possess the same order of the ellipsometric thickness with only 1Å difference (19Å and 18Å for

R1ArDT and **R1ArmDT** monolayers, respectively). The result therefore implied a similarity in the average chain tilt for both monolayers. In addition, this data may also suggest that **R1ArmDT** might occupy at the binding sites resemble and/or closely to those of **R1ArDT**, in which the inter-chain distances associated with chain-chain interactions for both monolayers would be in the same extent. The theoretical calculation demonstrates that the adsorption of both sulfur atoms of the 1,3-benzenedimethanethiol (1,3-**BDMT**) locates at the bridge site on the gold surface. Furthermore, it was reported that the distance between sulfur atoms for dithiolate head group in **R1ArDT** can span as far as 4.8Å without introducing bond-angle strain,[25] which is in the same extent of the intramolecular spacing between sulfur atoms in **R1ArmDT** (~4.43Å).

[0040] Other embodiments of the present invention teach that SAMs generated from the mono, and bidentate aromatic thiols are covalently bound to sulfur atoms on the gold surface. The XPS analysis for the peak positions of the S 2p region (shown in **Figure** 1) reveals that the SAMs generated from the mono, and bidentate aromatic thiols possess a binding energy of *ca.* 162-163.2 eV, indicating the presence of fully bound sulfur atoms on gold.[26] On the other hand, the SAM generated from the tritentate aromatic thiol, **R1ArTT**, displays the shoulder peak at ~164-165 eV, suggesting the incomplete binding of sulfur atoms on gold.[26,27] The deconvolution of S 2p spectrum of the **R1ArTT** SAM revealed the ~ 85% of all sulfur atoms bound to the gold surface. Furthermore, no oxidized sulfur species (*i.e.*, sulfoxide, and sulfone) at binding energy ~ 166-168 Ev[28] were detected for all monolayers, indicating the integrity of the monolayer formations.

[0041] Further XPS analysis on the peak integration ratios of S/Au[29] (data not shown) provides the information of molecular packing densities of the monolayers.[18,30,31] For example, in the present invention, the relative molecular packing densities of the monolayers are compared to the densely packed **C18** SAM as a reference, as shown in **Table 2**. (We noted that, for the adsorbates with a single chained tail group, the molecular packing density therefore reflect the chain packing density).

TABLE 2

Relative Molecular Densities, Relative Chain Packing Densities, and Possible Maximum Tilt Angles of SAMs Derived from C18 and New Classes of the Multidentate Aromatic Thiols Calculated from XPS Data

Adsorbate	Relative Molecular Packing Density*	Relative Chain Packing Density	Possible Maximum Tilt Angle (degree)
C18	100	100	30
R1ArMT	81	81	36
R1ArDT	63	63	43
R1ArmDT	55	55	47
R1ArTT	58	58	46
R2ArMT	68	136	23
R2ArDT	49	98	31
R3ArMT	44	132	24
R3ArDT	44	132	24

*** We estimate the experimental error in the packing density to be ±4%.**

[0042] Other embodiments of the present invention disclose that the relative molecular packing densities of the SAMs derived from single-tailed adsorbates decrease proportionally with a decrease of the chain-to-sulfur ratios. This is observed in **Series I** where the relative molecular packing densities of the SAMs decrease proportionally with an increase of the coordinated sulfur atoms. The trend of molecular packing density increases as follows: **R1ArMT** > **R1ArDT** > **R1ArTT**.

[0043] Other embodiments of the present invention teach that the increasing numbers of the hydrocarbon chains decreases molecular packing densities of the SAMs. This is observed in the comparisons of monolayers derived from the multi-tailed adsorbates (**R3ArMT**, **R2ArMT**, **R3ArDT**, and **R2ArDT**) with those derived from single-tailed adsorbates (**R1ArMT** and **R1ArDT**). For example, the molecular packing densities of SAMs generated from mono and bidentate adsorbates having one, two, and three tail groups increase as follows: **R1ArMT** > **R2ArMT** > **R3ArMT** and **R1ArDT** > **R2ArDT** > **R3ArDT**, respectively. On the other hand, the chain packing densities increase as follow: **R2ArMT** ~ **R3ArMT** > **R1ArMT** and **R3ArDT** > **R2ArDT** > **R1ArDT**, which show the corresponding values of 136%, 132%, and 82% for the former trend and 63%, 98%, and 132% for the later trend, respectively (shown in **Table 2**), due to the ratios of alkoxy chains to head groups for these adsorbates.

[0044] Accordingly, the trends of molecular packing densities for the monolayers derived from these mono and bidentate adsorbates can be clearly explained by the basis of the incommensurability between the thiolate head groups and the long hydrocarbon chain tail groups. The greater mismatch of the molecular counterparts requires the larger space for occupying the molecules, resulting in lower molecular packing densities.

[0045] Other embodiments of the present invention teach that the molecular packing density slightly decreases with longer intramolecular S····S distance. This is observed in the comparison of SAMs derived from **R1ArDT** and **R1ArmDT**, where the value of the molecular packing density of the latter monolayer is slightly lower when compared to that of the former monolayer. That can be partially attributed to the longer intramolecular S····S distance of **R1ArmDT**, which occupies a larger surface area than **R1ArDT**. Moreover, the results thus far imply that the orientation of the benzene ring in the **R1ArmDT** monolayer would be in an upright geometry; however, it would be more slightly tilted towards the metal surface than that in the **R1ArDT** monolayer. This can be attributed to the shorter distance between the benzene ring and the surface in the **R1ArmDT** film, leading to the partial contribution of the p-metal interaction on the formation of the monolayer which may induce and cause the tilt of the ring.[32,33]

[0046] Other embodiments of the present invention teach to analyze the orientation of the alkyl chains by comparing the relative chain packing densities of these monolayers. This is done by roughly estimating the possibility of the maximum chain tilts of these SAMs based on the molecular packing densities by using a densely packed **C18** monolayer with the chain tilt of 30 ° and by assuming that alkyls chains for SAMs in this study are fully-trans extended conformation. The estimated maximum chain tilts of SAMs derived from the new classes of multidentate aromatic thiols are shown in **Table 2**.

[0047] The possible maximum chain tilt of the **R1ArMT**, **R1ArDT**, and **R1ArTT** SAMs are approximately 36°, 43 °, and 46°, respectively (shown in **Table 2**). As mentioned above, the estimated chain tilts for the monolayers in this series point out that the tilt angles increase with increasing the molecular incommensurability between head group and the single chained tail group, namely sulfur-to-chain ratios. The occupying larger sizes of the multidentate head groups on the underlying gold surface creates void space between the alkyl chained tail groups. Thus, the tilts of alkyl chains increase in order to optimize inter-chain interactions. This interpretation is consistent with the chain tilt inferred from ellipsometric data and the results from PM-IRRAS and wettabilty experiments, which will be discussed in subsequent sections.

[0048] Based on the measured packing density of the tail groups and assuming that the alkyl chains are fully trans-extended, we can estimate the maximum possible tilt of the alkyl chains of **R1ArMT**, **R2ArMT**, and **R3ArMT** SAMs to be 36°, 23°, and 24°, respectively (shown in **Table 2**). This analysis suggests that the average tilt of the chains in these SAMs is distinct for each of the adsorbates examined and further distinct from the 30° chain tilt of normal alkanethiolate SAMs on gold.

Furthermore, the nature and magnitude of the tail group packing densities can influence both the assembly processes and the resultant structural quality of the films,[22,24,34,35] which will be discussed in the following sections.

[0049] Considering a densely chain packed **R3ArDT** monolayer (132%, relative to the **C18** SAM), the data suggests that **R3ArDT** might afford SAM with the reduction of chain tilt and less space area per chain as compared to other adsorbates. In the case of **R2ArDT**, given the chain-to-head group ratio of 1:1, the same as **C18**, a slight difference in chain packing density for the **R2ArDT** SAM (98%, relative to the **C18** SAM) implies that the alkyl chains in the **R2ArDT** SAM might be tilted approximately ~ 30 ° from the surface normal. On the other hand, the loosely chain and molecular packing densities for the monolayers derived from **R1ArDT**, due to the its incommensurability between the aromatic dithiolate headgroup and the single chained tail groups, give rise to a significant increase in the chain tilt. The possible maximum chain tilt of the **R1ArDT**, **R2ArDT**, and **R3ArDT** SAMs are approximately 43 °, 31 °, and 24 °, respectively. These interpretations are consistence with the previous studies, which have been reported that an increase of van der Waal diameters of tail group segments results in a reduced tilt angle.[36,37]

[0050] Due to its slightly lower chain packing density as compared to that of the **R1ArDT** monolayer, the **R1ArmDT** monolayer is expected to possess alkyl chains with a similar degree of chain tilt in the **R1ArDT** monolayer. The possible maximum chain tilts of the **R1ArDT** and **R1ArmDT** SAMs are approximately 43 ° and 46°, respectively. The calculated chain tilted point out that the alkyl chains for the **R1ArmDT** monolayer is more likely to have a higher exposure of methylene unit to the surface than that for the **R1ArDT** monolayer. This interpretation is strongly supported by the wettability data, which are discussed in the subsequent section.

[0051] Other embodiments of the present invention teach methods for analyzing the conformational order and orientation of SAMs using PM-IRRAS. PM-IRRAS affords conformational order and orientation information regarding organic thin films.[38-40] The frequency and band width of the methylene asymmetric C-H stretch ($\nu_a^{CH_2}$) are particularly sensitive to the degree of conformational order (crystallinity) of the hydrocarbon chains.[38] It is known that the densely packed and crystalline-like monolayer derived from **C18** displays the position of the $\nu_a^{CH_2}$ band at 2918 cm^{-1}. The shifts of this band to higher frequencies indicate less conformationally ordered monolayers.[38] PM-IRRAS spectra in C-H starching region of SAMs derived from the adsorbates in this study are shown in **Figure 2**.

[0052] The PM-IRRAS spectra for the monolayer films in **Series I** revealed that the $\nu_a^{CH_2}$ band for the **R1ArMT** SAM is located at the same position of 2918 cm^{-1} when compared to that for the **C18** monolayer, indicating a well-ordered structure of the **R1ArMT** SAM. On the other hand, the **R1ArDT** and **R1ArTT** SAMs possess broader bands and shift drastically to higher frequency at ~2926 and 2927 cm^{-1}, respectively. Furthermore, the orientation (*i.e.*, chain tilt) of the hydrocarbon chains can be qualitatively determined by the PM-IRRAS spectra. According to the surface selection rule, only the transition dipole moments that polarized and are perpendicular to the surface can be detected and observed in the vibrational spectrum.[38,41] In the case of monolayers derived from *n*-alkanethiols on gold with trans-extended alkyl chains containing an even number of carbon atoms, the dipole moment of the symmetric methyl stretching vibration ($\nu_s^{CH_3}$) is nearly perpendicular to the surface,[42,43] resulting in a significantly stronger intensity for the corresponding peak. With an increasing chain tilt from the surface normal, the intensity of the $\nu_s^{CH_3}$ will decrease and the chains will exhibit a greater exposure of methylene units to the surface.[2,43] The PM-IRRAS spectra in **Figure 2** demonstrate a substantial decrease in the intensities of the $\nu_s^{CH_3}$ bands in the monolayers derived from **R1ArDT** and **R1ArTT** when compared to those derived from **C18** and **R1ArMT**. Qualitatively, the degree of chain tilt for all these monolayers with respect to the $\nu_s^{CH_3}$ intensities increases in the following order: **C18** ~ **R1ArMT** > **R1ArDT** > **R1ArTT**. Additionally, the broader and enhanced intensities of $\nu_a^{CH_2}$ vibrational mode also support the conclusion that the presence of higher chain tilts and conformational disordering of the hydrocarbon chains in **R1ArDT** and **R1ArTT** monolayers is impacting the data, where a great number of $\nu_a^{CH_2}$ transition dipole moments are oriented along the surface normal due to the more random orientation of the methylene units.[41,44,45] However, it should be noted that PM-IRRAS suppresses signal from randomly oriented film components, leading to absolute intensities that can vary from sample to sample.[46,47] As a whole, the interpretations from the PM-IRRAS spectra are in good agreement with the results from the ellipsometric thickness measurements, and the packing densities of the monolayers investigated by XPS spectra and contact angle measurements.

[0053] For SAMs derived from **R1ArMT**, **R2ArMT**, and **R3ArMT**, the $\nu_{as}^{CH_2}$ and $\nu_s^{CH_2}$ bands for the SAM derived from **R1ArMT** appear at 2918 cm^{-1} and 2851 cm^{-1}, the same as that found for **C18**, indicating a crystalline-like conformational order for both films. The $\nu_{as}^{CH_2}$ bands of **R2ArMT** and **R3ArMT** films broaden and shift to higher frequency at 2923 and 2920 cm^{-1}, respectively. These results indicate that the SAMs derived from the double- and triple-chained adsorbates are less conformationally ordered than those derived from **C18** and **R1ArMT**. Overall, the IR data suggest the following order for the relative order/crystallinity of the SAMs: **C18** ~ **R1ArMT** > **R3ArMT** >>

R2ArMT. The data for the SAM derived from **R2ArMT** are particularly striking and indicate a liquid-like conformation for the alkyl chains. To discern the interplay of chain packing and orientation induced by the branched chains, further interpretation of the IR spectra is required. The $\nu_s^{CH}{}_3$ bands of the SAMs generated from **R2ArMT** and **R3ArMT** are more intense than those generated from **C18** and **R1ArMT**, which can be interpreted to indicate that the terminal methyl groups in the **R2ArMT** and **R3ArMT** SAMs are oriented more closely to the surface normal than those in the **C18** and **R1ArMT** SAMs. The broad region from 2890-2950 cm^{-1} arises from three overlapping components: the anti-symmetric methylene stretching band ($\nu_{as}^{CH}{}_2$ ~2918-2924 cm^{-1}) and the Fermi resonances (FR) of the symmetric methylene stretching band ($\nu_s^{CH}{}_2$ FR ~2890) and the symmetric methyl stretching band ($\nu_s^{CH}{}_3$ FR ~2940).[39,40,48,49] The Fermi resonance bands provide useful information regarding intermolecular interactions and chain assemblies. In the Raman spectra of *n*-alkanes, for example, Snyder et al. reported that the half-width of the $\nu_s^{CH}{}_3$ FR band is broader in the neat crystal than that in the isolated matrix,[49,50] which suggests that the bandwidth increases with increasing chain-chain interactions and chain packing.[39,40,48] Furthermore, the same phenomenon was observed for the $\nu_s^{CH}{}_2$ FR band in IR spectra, but the magnitude of the broadening was diminished because of a large difference in frequency between the fundamental and the binary state.[49] Qualitatively, the relative broadness of the Fermi resonances in **Figure 2** suggest that chain packing densities are greater in the SAMs derived from **R2ArMT** and **R3ArMT** than in the SAMs derived from **C18** and **R1ArMT**, which is consistent with our interpretation of the XPS data (vide supra). Another interesting observation is the decrease in the intensity of the bands related to methylene stretching in the **R2ArMT** and **R3ArMT** SAMs compared to the corresponding bands in the **C18** and **R1ArMT** SAMs. On the basis of the surface selection rules for IR spectroscopy, the intensities of both methylene stretching modes decrease with decreasing chain tilt.[45,51,52] Thus, the diminished intensity of the methylene stretching bands might indicate a smaller average tilt angle for the **R2ArMT** and **R3ArMT** SAMs than that in the **C18** and **R1ArMT** SAMs, assuming that all of the monolayers in are isotropic and composed of all trans-extended chains. Moreover, a reduced chain tilt (<30°) for the SAMs derived from **R2ArMT** and **R3ArMT** is in good agreement with the ellipsometric thickness data in **Table 1**, particularly when one considers the almost certainly poor molecular packing underneath the bulky aromatic units of **R2ArMT** and **R3ArMT**. However, despite the trends noted in the IR data here, we caution that changes in frequency, intensity, and bandwidth can arise from a variety of other factors, including chain deformations[53,54] and differences in the twist angles along the axis of the long alkyl chains.[55-57]

[0054] For SAMs derived from the new bidentate aromatic thiols, **R1ArDT**, **R2ArDT**, and **R3ArDT**, the positions of the $\nu_{as}^{CH_2}$ bands shift to higher wave numbers ~ 2925, 2923, and 2920 cm^{-1}, respectively. The two former SAMs represent the substantial shifts of the $\nu_{as}^{CH_2}$ bands, indicating that they are less crystalline in nature when compared to the later SAM where the $\nu_{as}^{CH_2}$ band shifted slightly higher (~ 2 cm^{-1}) relative to that of the crystalline-like conformational structure of the **C18** SAM. The lower crystallinity of the **R3ArDT** monolayer compared to the **C18** monolayer can be attributed to the structurally constrained hydrocarbon chains in the **R3ArDT** SAM, which might lead to partially disordered alignment of the chains. Therefore, based on the position of $\nu_{as}^{CH_2}$ band, the degree of conformation order of these monolayers decreases in the following order: **C18** > **R3ArDT** > **R2ArDT** > **R1ArDT**. Another interesting feature of the IR spectra in the C-H stretching region in **Figure 2** is the presence of the broad bands of the Fermi resonance of the symmetric methyl ($\nu_s^{CH_3}$ FR) appearing at ~ 2935 cm^{-1} in the spectra of the **C18** and **R3ArDT** monolayers. On the other hand, in the case of the **R1ArDT** and **R2ArDT** films, the contribution of the Fermi resonance bands are less significant and fully overlap with the $\nu_{as}^{CH_2}$ bands. It has been reported that the predominant Fermi resonance band is indicative of a strong chain-chain interactions.[39,40,48-50] Therefore, the results point out that the strong influence of the chain assembly interactions apparently exerts a greater impact on the monolayer films derived from the **C18** and **R3ArDT** monolayers, while presenting less influence on the **R1ArDT** and **R2ArDT** monolayers. Taking all IR results together, we discovered that the conformational order and the interplay of chain-chain interactions for the monolayers derived from these chelating adsorbates increase as the numbers of branched chains increase. This can be rationalized in terms of the chain packing density, namely chain-to-head group ratios, and commensurability between the dithiolate head group and branched chain tail groups. For example, in the case of the **R3ArDT** monolayer, the cross-sectional area of the triple-chained hydrocarbon branches is larger than the area occupied by the dithiolate head group on the gold surface, causing a loosely molecularly-packed monolayer and exhibiting less inter-chain interactions between two neighboring adsorbate chains. However, the presence of the well-ordered conformation of the hydrocarbon chains is due to the compensation of the intramolecular chain-to-chain interaction themselves among three long alkoxy chains, which is strongly supported by the PM-IRRAS and XPS data inferred by the $\nu_s^{CH_2}$ FR and a densely chain packing (132%), respectively. On the other hand, for the **R1ArDT** monolayer, the aromatic dithiolate head group is a mismatch to the single chain tail group, in which the cross-section area of the hydrocarbon chain is smaller relative to the area occupied by the head group. Although the molecular packing density of the **R1ArDT** monolayer is more densely relative to that of the **R2ArDT** and **R3ArDT** monolayers, the incommensurability between the head group and the single chain hydrocarbon in **R1ArDT** creates a larger void space above the phenyl ring. This causes a loosely chain packing with a higher chain tilt and deformation of the long alkoxy chains due to a reduction in chain assembly (*e.g.*, inter-and intramolecular chain-to-chain interactions). Given the ratio of the sulfur head group to the long alkoxy chains of 1:1, as is the case with **C18**, **R2ArDT** represents the chain packing density of 98%, which slightly deviate from the densely packed **C18** monolayer. Indeed, the addition of two long alkoxy chains improves the conformational order of the **R2ArDT** SAM when compared to that of **R1ArDT** SAM; however, it still presents a less ordered film than that of the **C18** SAM. These results can be attributed to the large dimension of the aromatic chelating head group and also to the void space between the double-branched chains that perturb the molecular packing density and diminish the chain-chain interactions of the **R2ArDT** SAM.

[0055] Compared with the peak characteristic of the $\nu_{as}{}^{CH}{}_2$ for the **C18** SAM, the broader bandwidth and higher intensities of the $\nu_{as}{}^{CH}{}_2$ bands with their position at higher frequencies ~ 2926 cm^{-1} for the **R1ArDT** and **R1ArmDT** SAMs indicated the deformation and disorder of the hydrocarbon chains (gauche conformation). Additionally, the barely visible peaks of the symmetric stretching mode of methyl ($\nu_s{}^{CH}{}_3$) bands also evidenced the gauche conformation of the hydrocarbon chains for these two monolayers. As judged by the IR characteristic spectra, the degree of conformational order and orientation of hydrocarbon chains for the **R1ArmDT** and the **R1ArDT** monolayers is indistinguishable. However, by taking all aforementioned results from chain and/or molecular packing density and contact angle measurements of these two monolayer systems, it is reasonable to suggest that the tilts of the hydrocarbon chain and/or the aromatic ring in the **R1ArmDT** monolayer is slightly higher than those in the **R1ArDT** monolayer.

[0056] Other embodiments of the present invention teach methods for obtaining informative data of conformational order and chain orientations of monolayer films using contact angle measurements.[58] The contact angles data is shown in **Table 3.**

TABLE 3

Advancing (θ_a) and Receding (θ_r) Contact Angles and Hysteresis ($\Delta\theta = \theta_a - \theta_r$) for Water ($H_2O$) for Hexadecane (HD), and Decalin (DEC) on Monolayer Films Generated from C18, and Multidentate Aromatic Adsorbates

Adsorbate	Contact Angle (degree)[*]								
	Water			Hexadecane			Decalin		
	θ_a	θ_r	$\Delta\theta$	θ_a	θ_r	$\Delta\theta$	θ_a	θ_r	$\Delta\theta$
C18	115	105	10	50	40	10	54	48	6
R1ArMT	115	105	10	50	40	10	54	48	6
R1ArDT	109	98	11	45	35	10	32	27	5
R1ArmDT	109	98	11	42	32	10	31	27	4
R1ArTT	107	97	10	42	32	10	27	20	7
R2ArMT	113	103	10	36	30	6	41	34	7
R2ArDT	111	101	10	42	32	10	38	32	6
R3ArMT	114	104	10	46	39	7	49	42	7
R3ArDT	113	103	10	44	34	10	47	37	10

[*] The average contact angles of water, hexadecane, and decalin were reproducible within ± 2 Å

The results of the advancing contact angles of water (θ_a^{H2O}) in Table 3 show an indication of the hydrophobic interfaces of all monolayers under the investigations. However, the sensitivity of water to probe hydrophobic monolayers is less than that of hydrocarbon solvents. Hexadecane is known to be a powerful tool for exploring the nanoscale of structural differences at the interfaces of hydrophobic films,[54,59] although it can partially intercalate through loosely packed monolayer.[18,60-62] This phenomenon causes the misleading interpretation for quality of monolayers. Our recent studies on interfacial wetting of SAMs derived from chelating adsorbates demonstrated that decalin is more applicable to analyze hydrocarbon films, especially loosely packed monolayers, than hexadecane.[62] This is due to its bulk steric molecular structure of decalin impeding the intercalation phenomena during the contact angle measurements.

[0057] For SAMs generated from multidentate adsorbates having a single chained tail group, the contact angle data in Table 3 demonstrates that the **R1ArTT** surface is more wettable by hexadecane and decalin than the **R1ArDT** surface, while the contact angle values of the **R1ArMT** SAM are apparently indistinguishable from the **C18** SAM, which is higher than those of the **R1ArDT** and **R1ArTT** SAMs. According to the atomic contact model, the results pointed out that the **R1ArTT** SAM exhibits a greater number of methylene units exposed to the interface with a higher degree of chain tilt when compared to the **R1ArDT** and **R1ArMT** SAMs. This interpretation is strongly supported by the tilt angles inferred by the XPS data. On the other hand, the interface of the **R1ArMT** monolayer consists mainly of the terminal methyl groups and is similar to the densely packed and well-ordered monolayer derived from **C18**. Therefore, the conformational order of the monolayers in this series can be estimated as follow: **C18** ~ **R1ArMT** > **R1ArDT** > **R1ArTT**.

[0058] In the case of SAMs generated from monodentate adsorbates having the varying numbers of alkoxy chained tail groups, **Table 3** shows that the contact angles for both hexadecane and decalin follow the same trend: **C18** ~ **R1ArMT** > **R3ArMT** >> **R2ArMT**. The fact that contact angles of water, hexadecane, and decalin are the same for the SAMs derived from **R1ArMT** and **C18** supports our proposal above that the packing and orientation of the **R1ArMT** SAM is similar to that of normal alkanethiolate SAMs. The reduced values for **R3ArMT** and particularly **R2ArMT** are somewhat surprising, but can be analyzed by considering both the packing density of the SAMs and the molecular structure of the adsorbates. Interestingly, the contact angle values of hexadecane (θ_a^{HD}) and decalin (θ_a^{DEC}) drop from their maximum values for the **R3ArMT** SAM and drop markedly lower for the **R2ArMT** SAM. This trend is inconsistent with the molecular packing densities measured by XPS, where the relative percent coverages are 100, 81, 68, and 44 for **C18**, **R1ArMT**, **R2ArMT**, and **R3ArMT**, respectively (vide supra). However, the corresponding tail group coverages are 100, 81, 136, and 132, respectively, due to the ratio of head group to tail groups for these adsorbates. Given that the contacting liquids probe the tail groups more than the head groups of these SAMs, we focus on the tail group packing density, orientation, and conformation to interpret the wettability data. As noted above regarding the XPS data, it is likely that the average tilt of the chains in the SAMs is distinct for each adsorbate. Despite this complication, it is still possible to infer structural/conformational information regarding the tail groups from the PM-IRRAS data. Specifically, the PM-IRRAS data indicate that the conformational order of the tail groups decreases as follows: **C18** ~ **R1ArMT** > **R3ArMT** >> **R2ArMT**. Importantly, the advancing contact angles of hexadecane and decalin follow the exact same trend (see **Table 3**). This correlation is consistent with a model in which the tail groups in the SAMs derived from **R3ArMT** and especially **R2ArMT** are less conformationally ordered (*i.e.*, possess more gauche conformations) and expose a higher fraction of methylene groups at the interface than the SAMs derived from **C18** and **R1ArMT**. As detailed previously, interfacial methylene groups are more wettable than interfacial methyl groups.[19]

[0059] For SAMs generated from bidentate adsorbates having varying numbers of tail groups (**R1ArDT**, **R2ArDT**, and **R3ArDT**), **Table 3** shows the unexpected and inconsistent results with no substantive difference in the interfacial wetting tested by hexadecane, in which θ_a^{HD} values fall within a range between about 42 ° and about 45 °. We hypothesized that hexadecane may partially intercalate through the void space between adsorbate molecules, long alkyl chains and/or monolayer[18,60,61] and interact with phenoxy adlayers, revealing θ_a^{HD} values which are found in the same extent for methoxyterminated SAMs.[63] On the other hand, the contact angle values of decalin can be used to distinguish the interfacial difference of the SAMs derived from these dithol adsorbates. The investigation of decalin wettability for these monolayers exhibits the interesting tendency that the θ_a^{DEC} values decrease with a decrease of the number of branched chains. Specifically, the data suggests the ability of the branched chains to fill the void space above the phenyl rings and to form more trans-extended conformations through van der Waal interactions between chains. Therefore, the conformational order of the long alkoxy chains were interpreted to decrease according to the trend as follows: **R3ArDT** > **R2ArDT** > **R1ArDT**.

[0060] The comparison of the contact angle values of SAMs generated from the different designs of the dithiolate head groups shows that the θ_a^{HD} for the **R1ArmDT** monolayer is 3 ° less than the values for the **R1ArDT** SAM, while the difference in the θ_a^{DEC} between these two monolayers is less pronounced. This might be ascribed to the lesser atomic contact of decalin when compared to that of hexadecane. As a whole, the lower values of contact angles for both testing liquids for the **R1ArmDT** SAM as compared to those for the **R1ArDT** SAM indicate that the former monolayer has a greater numbers of methylene units exposed at the interface than the later monolayer as a result of the slightly higher tilts of the aromatic ring and/or the long chain hydrocarbon (as discussed in the previous section).

[0061] Other embodiments of the present invention teach methods for evaluating the thermal stability of SAMs as a function of the numbers of branched chains and chelating head groups they contain. Stabilities of SAMs derived from selected adsorbates (**R1ArMT**, **R1ArDT**, **R1ArTT**, **R2ArDT**, **R3ArDT**, and **R1ArmDT**) are investigated by monitoring the solution-phase desorption in isooctane at 80 °C as a function of time. The extent of desorption is monitored by tracking the change in ellipsometric thicknesses. The desorption profiles illustrate the fraction of SAM remaining on the surface upon thermal treatment, as shown in **Figure 3**. All of the desorption profiles of the SAMs derived from the adsorbates in the present study except **R1ArmDT** clearly exhibit two distinct desorption regimes: (1) a fast initial desorption regimes described as the relatively steep slope as the period of time ~0-90 minutes; and (2) a slower/nondesorbing regime described as the gentle slope as the period of time ~90-240 minutes.

[0062] To quantitatively determine the relative rates of desorption in the fast desorbing regime, we evaluate the rate constant (k) for the desorption at 80 °C by fitting the data with the first order-kinetics according to equation 1:[54]

$$(T_t - T_\infty) / (T_0 - T_\infty) = e^{-kt} \qquad (1)$$

where $\mathbf{T}_t$ is the thickness of the monolayer at time **t**, and $\mathbf{T}_\infty$ is the thickness of the monolayer at the infinite time (~ 30 hours). **Table 4** shows the relative rate constants for the fast desorbing regimes and the fractions of SAM remaining on the surfaces for both distinct desorption regimes at the specific time at 90 and 240 minutes for the fast initial and the slow/non-desorbing regimes, respectively.

TABLE 4

Relative Rate Constants (k) for the Fast Desorbing Regime and the Fractions of SAM Remaining On the Surfaces for Both Desorption Regimes at the Specific Time of 90 and 240 Minutes for the Fast Initial and Slow/Non-Desorbing Regimes

Adsorbate	Fast Regime (0- 90 minutes)		Slow Regime (90-240 minutes)
	Remaining	Rate Constants $k \times 10^{-2}$ (min^{-1})	% SAM remaining
C18	27%	2.37	18%
R1ArMT	53%	0.99	32%
R1ArDT	46%	1.82	40%
R1ArmDT	94%	(a)	89%
R1ArTT	86%	0.10	78%
R2ArDT	52%	1.46	41%
R3ArDT	81%	0.42	54%

(a) The rate constant cannot be evaluated due to the insignificant change of the %SAM remaining.

In the case of slow/nondesorbing regime, desorption data cannot be fitted to obtain quantitative kinetic data because of the statistically insignificant changes in ellipsometric thickness which is in the experimental error range. The qualitative analysis of the relative thermal stability can be evaluated by comparing the remaining fraction of monolayers at arbitrary time in this regime. Therefore, the desorption profiles in this regime reflects thermodynamic rather than kinetic phenomena.

[0063] The desorption profiles of the SAMs derived from multidentate adsorbates having a single tail group (**Series I**) apparently illustrated that the **R1ArTT** SAM retains a higher degree of thermal desorption than the **R1ArMT**, and **R1ArDT** SAMs in both desorption regimes. Additionally, the **R1ArMT** SAM represented the greater thermal resistance of desorption than the **C18** SAM. This can be rationalized by the influence of additional π-π interactions between aromatic rings. Additionally, the steric repulsion of the aromatic ring can plausibly impede the intermolercular disulfide formation[21] for the **R1ArMT** SAM. Surprisingly, the rate constant of the desorption for the fast desorbing regime of the **R1ArMT** SAM is two times slower than that of the **R1ArDT** SAM, indicating that the **R1ArMT** SAM is more thermally stable than the **R1ArDT** SAM. Thus, the thermodynamic preference of the chelate effect and entropical disfavoring of desorption due to the intra- or intermolecular disulfide formations failed to correlate with the relative thermal stability of the **R1ArDT** monolayer upon the desorption process in the fast kinetic regime. This result can be rationalized on the basis of the structural features of the adsorbates. Prior molecular modeling of the spiro-dithiol head group demonstrated that the extended distance between two sulfur atoms can be spanned as far as 4.8Å without introducing excessive bond-angle strain.[25] Therefore, the S····S spacing of the spiro-dithiol head group on the gold surface is not commensurable to occupy the 3-fold hollow sites,[25] while our previous work proposed that the sulfur atoms of the monothiol adsorbate, **R1ArMT**, may likely bind to the 3-fold hollow sites of the Au(111) with a spacing of 4.99 Å, similarly to the sulfur atoms of **C18** bound onto the gold surface.[64,65]

[0064] According to the two distinct binding site models mentioned above, the restriction of access to the binding sites for both dithiolate head groups (*e.g.*, one sulfur atom on the 3-fold hollow and the other one on the top site of Au(111)) might contribute to a lower stability for the dithiol-based SAM. The influence of the restricted access to binding sites on thiolate desorption is supported by previous work from Walczak et al., who reported that alkanethiolate-based SAMs on gold substrates have been shown to desorb more readily from the terrace sites than from the step sites.[66] Additionally, the better relative crystallinity of the **R1ArMT** monolayer as compared to that of the **R1ArDT** monolayer should also influence desorption behavior. On the other hand, the most stable of the tridentate-based monolayer plausibly reveals that the entropy-driven chelating effect outweighs the bonding sites of sulfur atoms on gold lattice. In addition, the attachments of three sulfur atoms afford the **R1ArTT** SAM more thermodynamically stable than the **R1ArDT** SAM. For instance, considering the intramolecular desorption of the **R1ArDT** monolayer, the pathway would concurrently break two S-Au bonds to form disulfide formation. On the other hand, the intramolecular desorption of the **R1ArTT** monolayer is unfavorable, which can be explained by the fact that if two sulfur atoms would become unbound from the gold surface to form the cyclic disulfide product there is still one more sulfur atom bound to the surface. Furthermore, the cyclic disulfide formed by the desorption of two bound sulfur atoms from the gold surface can be readily reestablished to form on the surface.[67] Moreover, the intermoelucar desorptions of the **R1ArTT** monolayer are entropically disfavored more than those of the **R1ArDT** monolayer. For example, the **R1ArTT** monolayer requires the simultaneous breaking of six S-Au bonds, while in the case of the **R1ArDT** monolayer, only four S-Au bonds are needed for the formation of the dimer heterocycle. Therefore, the relative thermal stability of the monolayers in the fast kinetic regime can be concluded in the following trend: **R1ArTT** > **R1ArMT** > **R1ArDT** > **C18**.

[0065] For the slow/non desorbing kinetic regime, the remaining monolayer fractions of the SAMs derived from this series at 240 minutes decrease as follow: **R1ArTT** < **R1ArDT** < **R1ArMT**. Therefore, the relative long-term thermal stability of the monolayers can be concluded in the following trend: **R1ArTT** > **R1ArMT** > **R1ArDT** > **C18**, which correlated with the degree of chelation.

[0066] The desorption profiles (**Figure 3**) and rate constants (**Table 4**) revealed that the thermal stability of the SAMs obtained from the bidentate adsorbates in this study increases with increasing chain conformation inferred by the PM-IRRAS data. This result therefore indicates the key role of intramolecular chain-to-chain interactions to stabilize monolayers, in which the strength of chain assembled interactions is proportional to the numbers of molecular chains, namely the chain packing density. Consequently, we can rationalize the correlation between the desorption behavior and the degree of chain conformation, in which the most ordered conformation (implying strong van der Waals interactions) of the long alkoxy chains affords the most resistance to thermal desorption.[68,69] We therefore conclude that the thermal stability of these monolayers derived from the bidentate adsorbates increases as follow: **R1ArDT** > **R2ArDT** > **R3ArDT**.

[0067] The comparison of the thermal desorption profiles of the **R1ArmDT** and **R1ArDT** SAMs illustrates that the former SAM is more thermally stable as compared to the later SAM, in which the fraction of SAM remaining on the surface for the former SAM is significantly greater than that for the later SAM in both desorption regimes. Furthermore, the comparisons of the desorption profile of the **R1ArmDT** SAM with the other SAMs in this present study revealed that the monolayer derived from the specific design of extended dithiolate head group is even more thermally stable than those derived from tridentate aromatic thiol, **R1ArTT**, and other bidentate aromatic thiols (i.e. **R2ArDT** and **R3ArDT**). The greatest enhanced thermal stability of the **R1ArmDT** SAM is rationalized to the longer intramolecular S····S distance of the dithiolate head group of **R1ArmDT** which hinder the formation of the intramolecular cyclic disulfides upon the desorption process.

[0068] As a whole, the relative thermal stability of SAMs in this present study increases as follows: **R1ArmDT** > **R1ArTT** > **R3ArDT** > **R2ArDT** > **R1ArDT** > **R1ArDT** > **R1ArMT** > **C18**.

EXPERIMENTS OF THE INVENTION

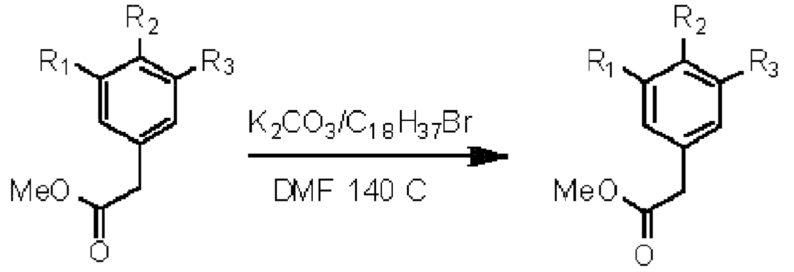
EXAMPLES

S1. Synthesis of the Intermediates used to Prepare Multidentate Aromatic Thiols with Varying Numbers of Hydrocarbon Chained Tail Group

[0069] The synthetic pathways used to prepare the intermediate compounds **1a** and **2a** for preparing the mono- and bidentate aromatic thiols (*i.e.*, **R1ArMT**, **R1ArDT**, **R2ArMT**, and **R2ArDT**), as well as the tridentate aromatic thiol, **R1ArTT**, shown in **Scheme S1**. For the intermediate compounds, **3g**, used to prepare **R3ArMT**, **R3ArDT**, and **R3ArTT**, the synthetic pathway is displayed in **Scheme S2**.

SCHEME S1

Synthetic Pathway of the Intermediate Compounds 1a and 2a, Used to Prepare R1ArDT, R2ArDT, and R1ArTT



1: R_1, R_2 = H, R_3 = OH
2: R_1, R_2 = OH, R_3 = H

1a: R_1, R_2 = H, R_3 = $OC_{18}H_{37}$, 90%
2a: R_1, R_2 = $OC_{18}H_{37}$, R_3 = H, 76%

4-Octadecyloxy-phenylacetate (1a)

[0070] A mixture of K_2CO_3 (8.31 g, 60.2 mmol), methyl 4-hydroxy-phenylacetate (5.00 g, 30.0 mmol) and 1-bromoctadecane (13.04 g, 39.11 mmol) in DMF (80 mL) was stirred at 140 °C overnight. After cooling to rt, K_2CO_3 was removed by filtration, and the filtrate was diluted with H_2O and acidified with 2 M HCl. The aqueous layer was extracted with CH_2Cl_2 (3×250 mL). The organic layers were combined and washed with H_2O (3×50 mL), dried over $MgSO_4$ and concentrated to dryness to afford the crude product. The crude product was taken up in CH_2Cl_2 and then cold MeOH was added to precipitate **1a** (11.30 g, 27.01 mmol, 90%) as white powder. ^1H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, $J = 6.9$ Hz, $ArOCH_2CH_2(CH_2)_{15}\mathit{CH_3}$, 3H), 1.26-1.41 (m, $ArOCH_2CH_2\mathit{(CH_2)_{15}}CH_3$, 30H), 1.73 (pent, $J = 7.4$ Hz, $ArOCH_2\mathit{CH_2}(CH_2)_{15}CH_3$, 2H), 3.56 (s, $Ar\mathit{CH_2}COOCH_3$, 2H), 3.68 ($ArCH_2COO\mathit{CH_3}$, 3H), 3.93 (t, $J = 6.9$ Hz, $ArO\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3}$, 2H), 6.85 (d, $J = 8.6$ Hz, $Ar\mathit{H}$, 2H), 7.17 (d, $J = 8.6$ Hz, $Ar\mathit{H}$, 2H).

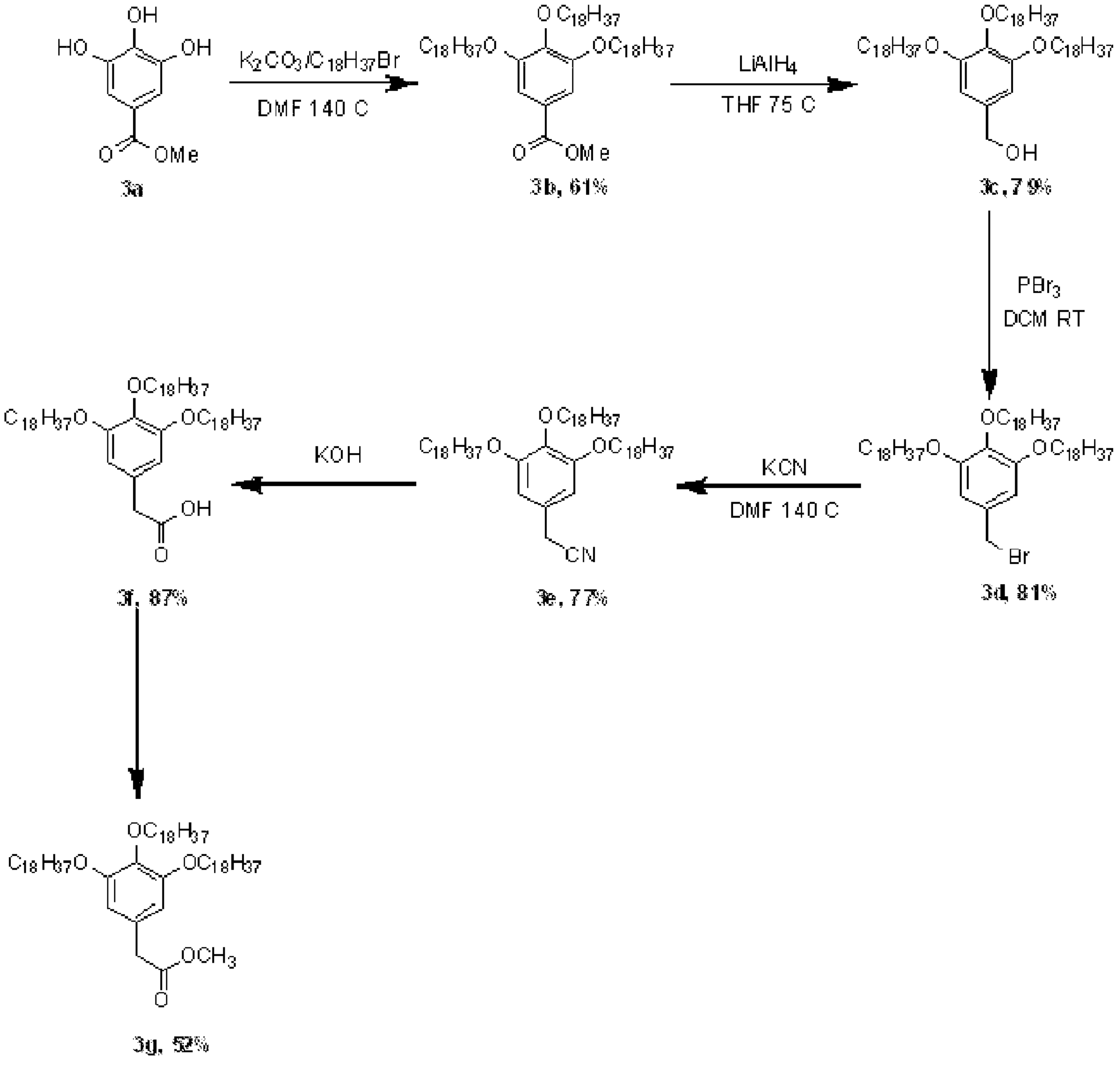
Methyl-2-(3,3-bis(octadecyloxy)phenyl)acetate (2a)

[0071] Following the procedures described for **1a**, methyl-2-(3,5-dihydroxyphenyl)acetate (2.50 g, 13.8 mmol) was treated with K_2CO_3 (18.97 g, 137.2 mmol) and 1-bromooctadecane (13.73 g, 41.16 mmol) in DMF (150 mL) at 120 °C to give a pale yellow crude product. The crude product was purified by column chomatography using CH_2Cl_2:hexane (3:2) as the eluent to afford a white powder product **2a** (7.21 g, 10.5 mmol, 76%). ^1H NMR (400 MHZ, $CDCl_3$): δ 0.87 (t, $J = 6.9$ Hz,

$\mathrm{Ar(OCH_2CH_2(CH_2)_{15}CH_3)_2}$, 6H), 1.24-1.43 (m, $\mathrm{Ar(OCH_2CH_2}\mathit{(CH_2)_{15}}\mathrm{CH_3)_2}$, 60H), 1.74 (pent, *J* = 7.8 Hz, $\mathrm{Ar(OCH_2}\mathit{CH_2}\mathrm{(CH_2)_{15}CH_3)_2}$, 4H), 3.53 (s, $\mathrm{Ar}\mathit{CH_2}\mathrm{COOCH_3}$, 2H), 3.70 (s, $\mathrm{ArCH_2COO}\mathit{CH_3}$, 3H), 3.90 (t, *J* = 6.9 Hz, $\mathrm{Ar(O}\mathit{CH_2}\mathrm{CH_2(CH_2)_{15}}\mathit{CH_3}\mathrm{)_2}$, 4H), 6.35 (s, Ar*H*, 1H), 6.39 (s, Ar*H*, 2H).

SCHEME S2

Synthetic Pathway of the Intermediate Compound 3g, Used to Prepare R3ArDT



Methyl-3,4,4-tris(octadecyloxy)benzoate (3b)

[0072] Following the procedure described for **1a**, methyl-3,4,5-trihydroxybenzoate (2.00 g, 10.9 mmol) was treated with K_2CO_3 (22.53 g, 163.0 mmol) and 1-bromooctadecane (16.30 g, 48.90 mmol) in DMF (250 mL) at 140 °C to give a pale yellow crude product. The crude product was purified by column chomatography using EtOAc:Hexane (1:4) as the eluent to afford **3b** as a white powder product (6.20 g, 6.58 mmol, 61%). ^{1}H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, *J* = 7.2 Hz,

$Ar(OCH_2CH_2(CH_2)_{15}\mathit{CH_3})_3$, 9H), 1.24-1.48 (m, $Ar(OCH_2CH_2\mathit{(CH_2)_{15}}CH_3)_3$, 90H), 1.68-1.81 (m, $Ar(OCH_2\mathit{CH_2}(CH_2)_{15}CH_3)_3$, 6H), 3.87 (s, $ArCO\mathit{CH_3}$, 3H), 3.98-4.01 (m, $Ar(O\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3})_3$, 6H), 7.24 (s, Ar*H*, 2H).

(3,4,5-Tris(octadecyloxy)phenyl)methanol (3c)

[0073] To a suspension of $LiAlH_4$ (0.60 g, 15 mmol) in THF (25 mL) was added dropwise a solution of **3b** (6.00 g, 5.03 mmol) in THF (20 mL). The reaction mixture was refluxed for 6 h under argon, quenched with water, and acidified with 2 M HCl. After being stirred for 10 min, the resultant mixture was extracted with CH_2Cl_2 (3×150 mL). The combined organic layers were washed subsequently with brine (3×50 mL) and water (3×50 mL), dried over $MgSO_4$, and evaporated to dryness to give **3c** (5.30 g, 5.80 mmol, 91%). ^1H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, *J* = 7.2 Hz, $Ar(OCH_2CH_2(CH_2)_{15}\mathit{CH_3})_3$, 9H), 1.24-1.47 (m, $Ar(OCH_2CH_2\mathit{(CH_2)_{15}}CH_3)_3$, 90H), 1.68-1.81 (m, $Ar(OCH_2\mathit{CH_2}(CH_2)_{15}CH_3)_3$, 6H), 3.63 (br, $ArCH_2OH$, 1H), 3.92-3.97 (m, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 6H), 4.59 (d, J = 5.7, $ArCH_2OH$, 2H), 6.55 (s, Ar*H*, 2H).

5-(Bromomethyl)-1,2,3-tris(octadecyloxy)benzene (3d)

[0074] A solution of PBr_3 (1.42 mL, 15.1 mmol) in CH_2Cl_2 (10 mL) was added slowly to a stirred solution of **3c** (4.60 g, 5.30 mmol) in CH_2Cl_2 (100 mL) at rt. The mixture was continually stirred for 3 h under argon, quenched with H_2O (25 mL), and extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were washed subsequently with brine (1×100 mL) and water (1×100 mL), and then dried over $MgSO_4$. Removal the solvents afforded **3d** (4.00 g, 4.10 mmol, 81%) as a white powder product. ^1H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, J = 6.9 Hz, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 9H), 1.24-1.47 (m, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 90H), 1.68-1.81 (m, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 6H), 3.92-3.96 (m, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 6H), 4.43 (s, $ArCH_2Br$, 2H), 6.56 (s, ArH, 2H).

2-(3,4,5-Tris(octadecyloxy)phenyl)acetonitrile (3e)

[0075] To a solution of **3d** (4.20 g, 4.30 mmol) in DMF (150 mL) was added a solution of NaCN (1.05g, 21.5 mmol) in water (15 mL). The mixture was heated at 140 °C for 72 h, quenched with water (50 mL), and extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were washed subsequently with brine (1×100 mL) and water (1×100 mL), and dried over $MgSO_4$. The solvent was removed to dryness to obtain the crude product. The crude product was dissolved in a minimum volume of CH_2Cl_2, and then cold MeOH was added to precipitate **3e** (3.13 g, 3.39 mmol, 79%). ^1H NMR (500 MHZ, $CDCl_3$): δ 0.88 (t, J = 6.9 Hz, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 9H), 1.24-1.47 (m, $Ar(OCH_2CH_2\mathit{(CH_2)_{15}}CH_3)_3$, 90H), 1.68-1.81 (m, $Ar(OCH_2\mathit{CH_2}(CH_2)_{15}CH_3)_3$, 6H), 3.65 (s, $Ar\mathit{CH_2}CN$, 2H), 3.92-3.96 (m, $Ar(O\mathit{CH_2}CH_2(CH_2)_{15}CH_3)_3$, 6H), 6.47 (s, Ar*H*, 2H).

2-(3,4,5-Tris(octadecyloxy)phenyl) acetic acid) (3f)

[0076] To a suspension of nitrile **3e** (2.00 g, 2.19 mmol) in methanol (150 mL) was added NaOH (30.0 g, 750 mmol) in water (20 mL). The mixture was heated to reflux for 72 h. When the reaction was cooled to rt, H_2O (100 mL) was poured to dilute the solution. The mixture was acidified by slowly adding conc. HCl to pH ~1 and then extracted with CH_2Cl_2 (3×150 mL). After washing of the combined organic layers with brine (2×100 mL) and water (1×100 mL), the organic phase was dried over $MgSO_4$ and evaporated to give the crude product. The crude product was taken up in CH_2Cl_2 and then cold MeOH was added to precipitate **3f** (1.80 g, 1.91 mmol, 87%). The product was used in the next step without further purification. ^{1}H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, *J* = 7.4 Hz, $Ar(OCH_2CH_2(CH_2)_{15}\mathit{CH_3})_3$, 9H), 1.24-1.49 (m, $Ar(OCH_2CH_2\mathit{(CH_2)_{15}}CH_3)_3$, 90H), 1.69-1.81 (m, $Ar(OCH_2\mathit{CH_2}(CH_2)_{15}CH_3)_3$, 6H), 3.48 (s, $Ar\mathit{CH_2}COOH$, 2H), 3.89-3.94 (m, $Ar(O\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3})_3$, 6H), 6.45 (s, Ar*H*, 2H).

Methyl-2-(3,4,5-tris(octadecyloxy)phenyl)acetate (3g)

[0077] A solution of 50% w/w BF_3 in MeOH (2,00 ml, 24.0 mmol) was added slowly under argon to a stirred solution of **3f** (4.00 g, 4.38 mmol) dissolved in a mixture of MeOH (50 mL) and THF (150 mL). The mixture was heated to reflux for 48 h. After cooled to room temperature, H_2O (50 mL) was added and the mixture was extracted with CH_2Cl_2 (3×150 mL). The collected organic layers were washed with brine (1×100 mL), water (1×100 mL), dried over $MgSO_4$, and evaporated to obtain ester **3g** as a pale yellow powder. Further purification by column chromatography with CH_2Cl:hexane (3:2), as the eluent afforded **3g** (2.20 g, 2.30 mmol, 52%) as a white solid. ^{1}H NMR (400 MHZ, $CDCl_3$): δ 0.86 (t, J = 6.9 Hz, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 9H), 1.18-1.50 (m, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 90H), 1.69-1.81 (m, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 6H), 3.51 (s, $ArCH_2COOCH_3$, 2H), 3.69 (s, $ArCH_2COOCH_3$, 3H), 3.89-3.96 (m, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 6H), 6.44 (s, ArH, 2H).

S2. Synthesis of the Aromatic Bidentate Thiols, R1ArDT, R2ArDT, and R3ArDT

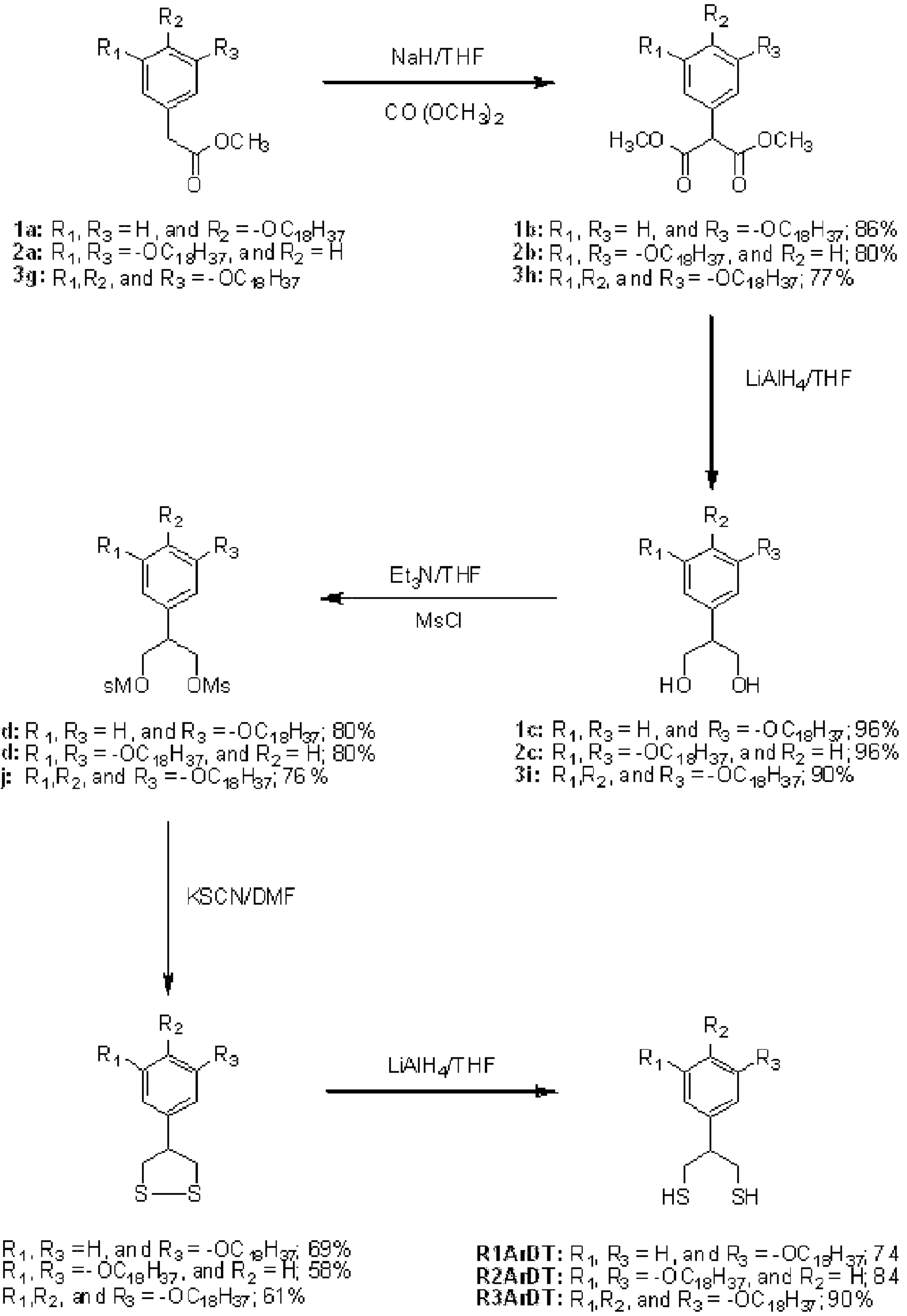
[0078] The synthetic pathway and procedure for synthesis of **R1ArDT**, **R2ArDT** and **R3ArDT** are presented in **Scheme S3.**

Dimethyl 2-(4-(octadecyloxy)phenyl)malonate (1b)

[0079] To a solution of **1a** (2.00 g, 12.0 mmol) in THF (25 mL) was placed sodium hydride (1.73 g, 72.21 mmol) at rt under argon. The mixture was stirred for 30 min, then treated with dimethyl carbonate (30 mL), and refluxed at 90 °C for 48 h. The resultant mixture was diluted with water (50 mL), neutralized with 2 M HCl, and extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were washed with water (1×100 mL), dried over $MgSO_4$ and evaporated under vacuum to obtain the crude product. The crude product was dissolved with a minimum volume of CH_2Cl_2 and then cold MeOH was added to the solution to precipitate **1b** (4.93 g, 10.3 mmol, 86%) as a white solid. ^1H NMR (300 MHZ, $CDCl_3$): δ 0.86 (t, $J = 6.9$ Hz, $ArOCH_2CH_2(CH_2)_{15}\mathit{CH_3}$, 3H), 1.25-1.44 (m, $ArOCH_2CH_2\mathit{(CH_2)_{15}}CH_3$, 30H), 1.75 (pent, $J = 7.8$ Hz, $ArOCH_2\mathit{CH_2}(CH_2)_{15}CH_3$, 2H), 3.73 (s, $Ar(CH(COO\mathit{CH_3})_2)$, 6H), 3.92 (t, $J = 6.9$ Hz, $ArO\mathit{CH_2}CH_2(CH_2)_{15}CH_3$, 2H), 4.57 (s, Ar $(C\mathit{H}(COOCH_3)_2)$, 6.86 (d, $J = 8.7$ Hz, Ar*H*, 2H), 7.28 (d, $J = 8.7$ Hz, Ar*H*, 2H).

SCHEME S3

Synthetic Pathway of R1ArDT, R2ArDT, and R3ArDT



2-(4-(Octadecyloxy)phenyl)propane-1,3-diol (1c)

[0080] To a suspension of $LiAlH_4$ (0.80 g, 20 mmol) in THF (15 mL) was added slowly a solution of **1b** (2.00 g, 4.19 mmol) via addition funnel under argon. The mixture was refluxed for 6 h, cooled down to rt, quenched with ethanol (25 mL) and acidified to pH ~1 with 2 M HCl. The mixture was extracted with diethyl ether (3×150 mL). The combined organic layers were subsequently washed with a dilute HCl solution (1×100 mL), brine (1×100 mL), and water (1×100 mL), and then dried over $\mathrm{MgSO_4}$. Removal of the organic solvent under vacuum gave the crude product, which was purified by co-solvent recrystallization with $\mathrm{CH_2Cl_2}$ and MeOH to afford **1c** (1.70 g, 4.04 mmol, 96%) as a white powder. ^{1}H NMR (400 MHZ, $\mathrm{CDCl_3}$): δ 0.87 (t, J = 6.5 Hz, $\mathrm{ArOCH_2CH_2(CH_2)_{15}}\mathit{CH_3}$, 3H), 1.24-1.45 (m, $\mathrm{ArOCH_2CH_2}\mathit{(CH_2)_{15}}\mathrm{CH_3}$, 30H), 1.76 (pent, J = 8.0 Hz, $\mathrm{ArOCH_2}\mathit{CH_2}\mathrm{(CH_2)_{15}CH_3}$, 2H), 3.15 (m (br), Ar $\mathrm{(CH(CH_2}\mathit{OH}\mathrm{)_2)}$, 2H), 3.95 (m, $\mathrm{ArO}\mathit{CH_2}\mathrm{CH_2(CH_2)_{15}CH_3}$, $\mathrm{Ar(C}\mathit{H}\mathrm{(CH_2OH)_2)}$, and Ar $\mathrm{(CH(}\mathit{CH_2}\mathrm{OH)_2)}$, 7H), 6.89 (d, J = 8.4 Hz, ArH, 2H), 7.17 (d, J = 8.4 Hz, ArH, 2H).

2-(4-(Octadecyloxy)phenyl)propane-1,3-dimethanesulfonate (1d)

[0081] To a stirred solution of **1c** (2.00 g, 4.76 mmol), and triethylamine (3.98 mL, 28.6 mmol) in anhydrous THF (25 mL) was added dropwise methansulfonyl chloride (2.22 mL, 28.6 mmol) over 5 min under argon atmosphere. After the addition was completed, stirring was continued for 4 hr at rt. Ice cold water was poured into the reaction mixture to destroy any excess methansulfonyl chloride. The mixture was extracted with diethyl ether (3×100 mL). The combined organic layers were washed with dilute HCl (1×100 mL), brine (1×100 mL), and water (1×100 mL). The organic phase was dried over $\mathrm{MgSO_4}$ and removed under vacuum to give the crude mesylate **1d**. The crude product was dissolved with a minimum volume of $\mathrm{CH_2Cl_2}$ and then MeOH was added to the solution to precipitate **1d** (2.2 g, 3.82 mmol, 80%) as a white solid. ^{1}H NMR (300 MHZ, $\mathrm{CDCl_3}$): δ 0.88 (t, J = 6.9 Hz, $\mathrm{ArOCH_2CH_2(CH_2)_{15}}\mathit{CH_3}$, 3H), 1.25-1.44 (m, $\mathrm{ArOCH_2CH_2}\mathit{(CH_2)_{15}}\mathrm{CH_3}$, 30H), 1.77 (pent, J = 7.8 Hz, $\mathrm{ArOCH_2}\mathit{CH_2}\mathrm{(CH_2)_{15}CH_3}$, 2H), 2.96 (s, $\mathrm{ArCH(CH_2SO_2}\mathit{CH_3}\mathrm{)_2}$, 9H), 3.45 (m, $\mathrm{ArC}\mathit{H}\mathrm{(CH_2SO_2CH_3)_2}$, 1H), 3.93 (t, J = 6.6 Hz, $\mathrm{ArO}\mathit{CH_2}\mathrm{CH_2(CH_2)_{15}}\mathit{CH_3}$, 2H), 4.50 (t, J = 6.3 Hz, $\mathrm{ArCH}\mathit{(CH_2}\mathrm{SO_2CH_3)_2}$, 1H), 6.87 (d, J = 9.0 Hz, ArH, 2H), 7.17 (d, J = 9.0 Hz, ArH, 2H).

4-(4-(Octadecyloxy)phenyl)-1,2-dithiolane (1e)

[0082] A mixture of **1d** (1.50 g, 2.60 mmol) and KSCN (5.06 g, 52.0 mmol) in a mixture solution of EtOH (10 mL) and DMF (10 mL) was stirred at 140 °C for 24 h. The resulting brownish solution was poured into cold water. The precipitate formed was filtrated, washed with water, and then dissolved in $\mathrm{CH_2Cl_2}$ (250 mL). The organic layer was washed with saturated brine (1×50 mL), dried over $\mathrm{MgSO_4}$ and concentrated to dryness. The crude product was purified by column chromatography on silica gel, eluting with $\mathrm{CH_2Cl_2}$ to afford **1d** (0.81 g, 1.79 mmol, 69%). ^{1}H NMR (500 MHZ, $\mathrm{CDCl_3}$): δ 0.87 (t, J = 6.9 Hz, $\mathrm{ArOCH_2CH_2(CH_2)_{15}}\mathit{CH_3}$, 3H), 1.25-1.46 (m, $\mathrm{ArOCH_2CH_2}\mathit{(CH_2)_{15}}\mathrm{CH_3}$, 30H), 1.78 (pent, $J = 8.0$ Hz, $ArOCH_2\mathit{CH_2}(CH_2)_{15}CH_3$, 2H), 3.26-3.42 (m, $ArC\mathit{H}(CH_2S)_2$ and $ArCH(\mathit{CH_2}S)_2$, 5H), 3.94 (t, $J = 6.9$ Hz, $ArO\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3}$, 2H), 6.92 (d, $J = 8.6$ Hz, $Ar\mathit{H}$, 2H), 7.12 (d, $J = 8.6$ Hz, $Ar\mathit{H}$, 2H).

2-(4-(Octadecyloxy)phenyl)propane-1,3-dithiol (R1ArDT)

[0083] A solution of **1e** (2.00 g, 4.43 mmol) in THF (25 ml) was added dropwise into a suspension solution of $LiAlH_4$ (0.84 g, 22 mmol) in THF (10 mL) through an addition funnel argon. The mixture was stirred at rt for 6 h, quenched with ethanol (25 mL), then acidified with 2 M HCl (previously degas by bubbling with argon). After stirred for 10 min, the mixture was extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were washed with brine (1×100 mL) and water (1×100 mL), dried over $MgSO_4$, and evaporated to dryness to give **R1ArDT** (1.50 g, 3.31 mmol, 74%). ^1H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, $J = 6.9$ Hz, $ArOCH_2CH_2(CH_2)_{15}\mathit{CH_3}$, 3H), 1.25-1.48 (m, $ArOCH_2CH_2\mathit{(CH_2)_{15}}CH_3$, and $ArCH(CH_2\mathit{SH})_2$, 32H), 1.76 (pent, $J = 8.0$ Hz, $ArOCH_2\mathit{CH_2}(CH_2)_{15}CH_3$, 2H), 2.84-2.87 (m, $ArCH(CH_2\mathit{SH})_2$ and $ArC\mathit{H}(CH_2SH)_2$, 5H), 3.93 (t, $J = 6.9$ Hz, $ArO\mathit{CH_2}CH_2(CH_2)_{15}CH_3$, 2H), 6.89 (d, $J = 8.6$ Hz, $Ar\mathit{H}$, 2H), 7.14 (d, $J = 8.6$ Hz, $Ar\mathit{H}$, 2H). ^{13}C NMR (125 MHZ, $CDCl_3$): δ 14.22, 22.79, 26.16, 29.53, 29.70, 32.02, 51.38, 68.07, 114.71, 128.90, 132.98, 158.92.

Dimethyl 2-(3,5-bis(octadecyloxy)phenyl)malonate (2b)

[0084] Following the procedure described for **1b.** To a reaction mixture of **2a** (1.00 g, 1.45 mmol) and sodium hydride (0.21 g, 8.73 mmol) in THF (20 mL) was added dropwise dimethyl carbonate (30 mL) to obtain diester **2b** (0.87 g, 1.16 mmol, 80%) as a white powder product. ^1H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, $J = 6.9$ Hz, $Ar(OCH_2CH_2(CH_2)_{15}\mathit{CH_3})_2$, 6H), 1.24-1.43 (m, $Ar(OCH_2CH_2\mathit{(CH_2)_{15}}CH_3)_2$, 60H), 1.74 (pent, $J = 8.0$ Hz, $Ar(OCH_2\mathit{CH_2}(CH_2)_{15}CH_3)_2$, 4H), 3.74 (s, $ArCH(CH_2CO\mathit{CH_3})_2$, 6H), 3.91 (t, $J = 6.3$ Hz, $Ar(O\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3})_2$, 4H), 4.54 (s, $ArC\mathit{H}(COOCH_3)_2$, 1H), 6.40 (s, $Ar\mathit{H}$, 1H), 6.51 (s, $Ar\mathit{H}$, 2H).

2-(3,5-Bis(octadecyloxy)phenyl)propane-1,3-diol (2c)

[0085] Following the procedure described for **1c**. To a suspension of $LiAlH_4$ (0.38 g, 10 mmol) in THF (10 mL) was added a solution of **2b** (1.50 g, 2.01 mmol) in THF (15 mL) to obtain **2c** (1.34 g, 1.94 mmol, 96%) as a white powder. ^1H NMR (400 MHZ, $CDCl_3$): δ 0.87 (t, $J = 6.8$ Hz, $Ar(OCH_2CH_2(CH_2)_{15}\mathit{CH_3})_2$, 6H), 1.24-1.43 (m, $Ar(OCH_2CH_2\mathit{(CH_2)_{15}}CH_3)_2$, 60H), 1.74 (pent, $J = 7.8$ Hz, $Ar(OCH_2\mathit{CH_2}(CH_2)_{15}CH_3)_2$, 4H), 3.05 (br, Ar $(CH(CH_2\mathit{OH})_2)$, 2H), 3.90-3.95 (m, $ArC\mathit{H}(CH_2OH)_2$, $ArCH(\mathit{CH_2}OH)_2$, and $Ar(O\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3})_2$, 6H), 6.34 (s, $Ar\mathit{H}$, 2H).

2-(3,5-Bis(octadecyloxy)phenyl)propane-1,3-diyl dimethanesulfonate (2d)

[0086] Following the procedure described for **1d**. A mixture of **2c** (1.50 g, 2.17 mmol) and triethylamine (1.82 mL, 13.1 mmol) in THF (30 mL) was treated with methansulfonyl chloride (1.02 mL, 13.1 mmol) to obtain the crude mesylate **2d** (1.48 g, 1.75 mmol, 80%) as a white powder product. The crude product was directly used in the next step without any further purification. ^{1}H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, J = 6.8 Hz, $Ar(OCH_2CH_2(CH_2)_{15}\mathit{CH_3})_2$, 6H), 1.25-1.49 (m, $Ar(OCH_2CH_2\mathit{(CH_2)_{15}}CH_3)_2$, 60H), 1.77 (pent, J = 7.4 Hz, $Ar(OCH_2\mathit{CH_2}(CH_2)_{15}CH_3)_2$, 4H), 2.97 (s, $ArCH(CH_2SO_2\mathit{CH_3})_2$, 6H), 3.36 (m, $ArC\mathit{H}(CH_2SO_2CH_3)_2$, 1H), 3.90 (t, J = 6.9 Hz, $ArO(\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3})_2$, 4H), 4.54-4.49 (m, $ArCH(\mathit{CH_2}SO_2CH_3)_2$, 4H), 6.34 (s, Ar*H*, 2H), 6.39 (s, Ar*H*, 1H).

4-(3,5-Bis(octadecyloxy)phenyl)-1,2-dithiolane (2e)

[0087] Following the procedure described for **1e**. The mesylate **2d** (1.50 g, 1.77 mmol) was treated with KSCN (3.45 g, 35.5 mmol) in a mixture solution of EtOH (10 mL) and DMF (10 mL). The crude product was purified by column chromatography using CH_2Cl_2:hexanes (3:2) as the eluent to afford **2e** (0.74 g, 1.0 mmol, 58%). ^{1}H NMR (300 MHZ, $CDCl_3$): δ 0.87 (t, J = 7.3 Hz, $Ar(OCH_2CH_2(CH_2)_{15}\mathit{CH_3})_2$, 6H), 1.25-1.49 (m, $Ar(OCH_2CH_2\mathit{(CH_2)_{15}}CH_3)_2$, 60H), 1.77 (pent, J = 8.2 Hz, $Ar(OCH_2\mathit{CH_2}(CH_2)_{15}CH_3)_2$, 4H), 3.26-3.43 (m, $ArCH(\mathit{CH_2}S)_2$, and $Ar\mathit{CH}(CH_2S)_2$, 5H), 3.90 (t, J = 6.9 Hz, $ArO(\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3})_2$, 4H), 6.31 (s, Ar*H*, 2H), 6.42 (s, Ar*H*, 1H).

2-(3,5-Bis(octadecyloxy)phenyl)propane-1,3-dithiol (R2ArDT)

[0088] Following the procedure described for **R1ArDT**. To a suspension of $LiAlH_4$ (0.13 g, 3.5 mmol) in THF (10 mL) was added dropwise a solution of **2e** (0.50 g, 0.70 mmol) in THF (15 mL) to yield the **R2ArDT** (0.42 g, 0.58 mmol, 84%). ^{1}H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, J = 6.9 Hz, $Ar(OCH_2CH_2(CH_2)_{15}\mathit{CH_3})_2$, 6H), 1.25-1.49 (m, $Ar(OCH_2CH_2\mathit{(CH_2)_{15}}CH_3)_2$ and $ArCH(CH_2\mathit{SH})_2$, 62H), 1.77 (pent, J = 8.0 Hz, $Ar(OCH_2\mathit{CH_2}(CH_2)_{15}CH_3)_2$, 4H), 2.85 (m, $ArCH(\mathit{CH_2}SH)_2$ and $Ar\mathit{CH}(CH_2SH)_2$, 5H), 3.90 (t, J = 6.3 Hz, $ArO(\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3})_2$, 4H), 6.30 (s, Ar*H*, 2H), 6.34 (s, Ar*H*, 1H). ^{13}C NMR (125 MHZ, $CDCl_3$): δ 14.22, 22.79, 26.16, 29.52, 29.71, 32.02, 52.66, 68.14, 99.80, 106.54, 144.52, 160.58.

Dimethyl 2-(3,4,5-tris(octadecyloxy)phenyl)malonate (3h)

[0089] Following the reaction described for **1b**. To a reaction mixture of **3g** (2.00 g, 2.09 mmol) and sodium hydride (0.30 g, 12.6 mmol) in THF (20 mL) was added dropwise dimethyl carbonate (30 mL) to obtain **3h** (1.64 g, 1.62 mmol, 77%). ^{1}H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, J = 6.9 Hz, $Ar(OCH_2CH_2(CH_2)_{15}\mathit{CH_3})_3$, 9H), 1.18-1.49 (m, $Ar(OCH_2CH_2\mathit{(CH_2)_{15}}CH_3)_3$, 90H), 1.69-1.83 (m, $Ar(OCH_2\mathit{CH_2}(CH_2)_{15}CH_3)_3$, 6H), 3.75 (s, $ArCH(CH_2CO\mathit{CH_3})_2$, 6H), 3.91-3.96 (m,

$Ar(OCH_2CH_2(CH_2)_{15}CH_3)_2$, 6H), 4.51 (s, $ArCH(COOCH_3)_2$, 1H), 6.56 (s, ArH, 2H).

2-(3,4,5-Tris(octadecyloxy)phenyl)propane-1,3-diol (3i)

[0090] Following the reaction described for **1c**. To a suspension of $LiAlH_4$ (0.28 g, 7.4 mmol) in THF (10 mL) was added a solution of **3h** (1.50 g, 1.48 mmol) in THF (15 mL) to obtain **3i** (1.28 g, 1.33 mmol, 90%). ^1H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, $J = 6.9$ Hz, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 9H), 1.25-1.49 (m, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_2$, 90H), 1.69-1.80 (m, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 6H), 3.81-3.93 (m, $ArCH(CH_2OH)_2$, $ArCH(CH_2OH)_2$, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 9H), 6.39 (s, ArH, 2H).

2-(3,4,5-Tris(octadecyloxy)phenyl)propane-1,3-diyl dimethanesulfonate (3j)

[0091] Following the procedure described for **1d.** A mixture of **3i** (1.00 g, 1.04 mmol) and triethylamine (0.87 mL, 6.3 mmol) in THF (30 mL) was treated with methansulfonyl chloride (0.49 mL, 6.3 mmol) to obtain the crude mesylate **3j** (0.89 g, 0.80 mmol, 76%) as a white powder product. The crude product was directly used in the next step without any further purification. ^1H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, $J = 7.4$ Hz, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 9H), 1.25-1.49 (m, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 90H), 1.70-1.80 (m, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 6H), 2.95 (s, $ArCH(CH_2SO_2CH_3)_2$, 6H), 3.35 (m, $ArCH(CH_2SO_2CH_3)_2$, 1H), 3.90-3.94 (m, $ArO(CH_2CH_2(CH_2)_{15}CH_3)_3$, 6H), 4.54-4.47 (m, $ArCH(CH_2SO_2CH_3)_2$, 4H), 6.40 (s, ArH, 2H).

4-(3,4,5-Tris(octadecyloxy)phenyl)-1,2-dithiolane (3k)

[0092] Following the procedure described for **1e.** The mesylate **3j** (1.00 g, 0.90 mmol) was treated with KSCN (1.75 g, 18.0 mmol) in a solution mixture of EtOH (10 mL) and DMF (10 mL). The crude product was purified by column chromatography using hexanes:EtOAc (4:1) as the eluent to afford **3k** (0.54 g, 0.55 mmol, 61%). ^1H NMR (400 MHZ, $CDCl_3$): δ 0.87 (t, $J = 6.9$ Hz, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 9H), 1.25-1.49 (m, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 90H), 1.70-1.80 (m, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 6H), 3.27-3.40 (m, $ArCH(CH_2S)_2$ and $ArCH(CH_2S)_2$, 5H), 3.90-3.94 (m, $ArO(CH_2CH_2(CH_2)_{15}CH_3)_3$, 6H), 6.34 (s, ArH, 2H).

2-(3,5-Bis(octadecyloxy)phenyl)propane-1,3-dithiol (R3ArDT)

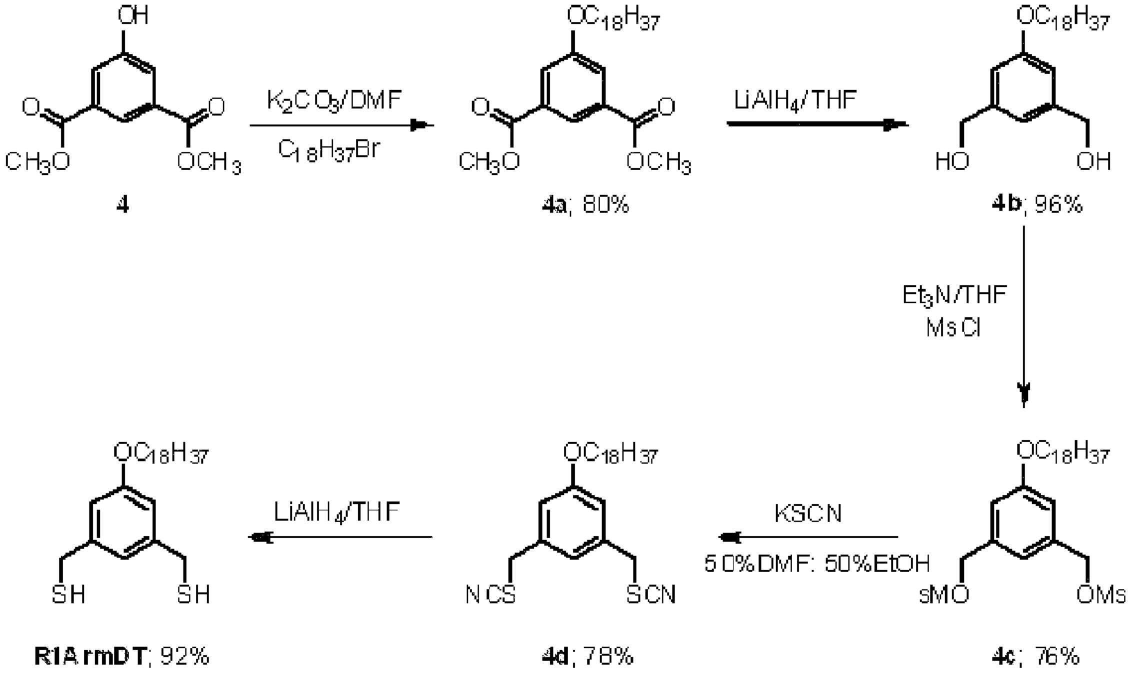
[0093] Following the procedure described for **R1ArDT**. To a suspension of $LiAlH_4$ (0.04 g, 1.01 mmol) in THF (10 mL) was added dropwise a solution of **3k** (0.20 g, 0.20 mmol) in THF (15 mL) to yield **R3ArDT** (0.18 g, 0.18 mmol, 90%). ^1H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, $J = 6.3$ Hz, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 9H), 1.25-1.48 (m, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$ and $ArCH(CH_2SH)_2$, 90H), 1.70-1.80 (m, $Ar(OCH_2CH_2(CH_2)_{15}CH_3)_3$, 6H), 2.83-2.85 (m, $ArCH(CH_2SH)_2$ and $ArCH(CH_2S)_2$, 5H), 3.91-3.94 (m, $ArO(CH_2CH_2(CH_2)_{15}CH_3)_3$, 6H), 6.33 (s, ArH, 2H). ^{13}C NMR (125 MHZ, $CDCl_3$): δ 14.24, 22.80, 26.21, 29.48, 29.56, 29.76, 29.83, 30.44, 32.03, 52.46, 69.31, 73.47, 106.40, 136.19, 137.48, 153.30.

S3. Synthesis of 4,6-Bis(octadecyloxy)-1,3-phenylene)dimethanethiol (R1ArmDT)

[0094] The synthetic pathway and procedure for synthesis of (4,6-bis(octadecyloxy)-1,3-phenylene)dimethanethiol, **R1ArmDT** are presented in **Scheme S4**.

SCHEME S4

Synthetic pathway of R1ArmDT



Dimethyl 5-(octadecyloxy)isophthalate (4a)

[0095] A mixture of 1-bromoctadecane (4.12 g, 12.37 mmol), dimethyl 5-hydroxyisophthalate (2.00 g, 9.52 mmol), and K_2CO_3 (2.63 g, 19.0 mmol) in DMF (150mL) was stirred at 120 °C for overnight. After cooling, K_2CO_3 was removed by filtration, and then the filtrate was diluted with H_2O and acidified with 2 M HCl. The aqueous layer was extracted with CH_2Cl_2 (3×250 mL). The organic layers were combined and washed with H_2O (3×50 mL), dried over $MgSO_4$, and concentrated to dryness to afford the crude product. The crude product was chromatographed on silica gel using a mixture of CH_2Cl_2 and hexane (3:2) as the eluent to give **4a** (3.52 g, 7.61 mmol, 80%) as a white powder product. ^{1}H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, J = 6.9 Hz, $ArOCH_2CH_2(CH_2)_{15}\mathit{CH_3}$, 3H), 1.26-1.46 (m, $ArOCH_2CH_2\mathit{(CH_2)_{15}}CH_3$, 30H), 1.80 (pent, J = 6.9 Hz, $ArOCH_2\mathit{CH_2}(CH_2)_{15}CH_3$, 2H), 3.94 (s, $Ar(COO\mathit{CH_3})_2$, 6H), 4.02 (t, J = 6.9 Hz, $ArO\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3}$, 2H), 7.73 (s, Ar*H*, 2H), 8.25 (Ar*H*, 2H).

(5-(Octadecyloxy)-1,3-phenylene)dimethanol (4b)

[0096] A solution of **4a** (3.00 g, 6.48 mmol) in THF (20 mL) was added dropwise to a suspension of $LiAlH_4$ (0.62 g, 16 mmol) in THF (25mL) under argon. The reaction was stirred and heated to reflux for 6 h, then quenched with H_2O, and acidified with 2 M HCl. The mixture was extracted with diethyl ether (3×150 mL). The combined organic layers were washed with brine (1×100 mL) and water (1×100 mL), dried over $MgSO_4$, and evaporated to dryness. The crude product was taken up in CH_2Cl_2 and then cold MeOH was added to precipitate **4b** (2.54 g, 6.25 mmol, 96%) as white solid. ^{1}H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, J = 6.9 Hz, $ArOCH_2CH_2(CH_2)_{15}\mathit{CH_3}$, 3H), 1.26-1.45 (m, $ArOCH_2CH_2\mathit{(CH_2)_{15}}CH_3$, 30H), 1.63 (t, J = 4.6 Hz, $Ar(CH_2O\mathit{H})_2$, 2H) 1.77 (pent, J = 7.4 Hz, $ArOCH_2\mathit{CH_2}(CH_2)_{15}CH_3$, 2H), 3.96 (t, J = 6.9 Hz, $ArO\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3}$, 2H), 4.66 (d, J = 4.6 Hz, $Ar(\mathit{CH_2}OH)_2$, 4H), 6.81 (s, Ar*H*, 2H), 6.93 (Ar*H*, 2H).

(5-(Octadecyloxy)-1,3-phenylene)bis(methylene) dimethanesulfonate (4c)

[0097] Methansulfonyl chloride (1.15 mL, 14.8 mmol) was added dropwise over 5 min to a stirred solution of **4b** (2.00 g, 4.92 mmol) and triethylamine (2.06 mL, 14.8 mmol) in anhydrous THF (25 mL) under argon. The mixture was stirred for 4 h at rt. To destroy excess methansulfonyl chloride, ice-cold water was added to the reaction flask. The mixture was extracted with diethyl ether (3×100 mL). The organic layers were washed successively with 2M HCl (1×100 mL) and water (1×100 mL), dried over $MgSO_4$, and concentrated to dryness to yield the crude mesylate **4c**. The crude product was dissolved with a minimum volume of CH_2Cl_2 and cold MeOH was added to precipitate **4c** (2.19 g, 3.73 mmol, 76%). ^{1}H NMR (400 MHZ, $CDCl_3$): δ 0.87 (t, J = 6.9 Hz, $ArOCH_2CH_2(CH_2)_{15}\mathit{CH_3}$, 3H), 1.25-1.45 (m, $ArOCH_2CH_2\mathit{(CH_2)}_{15}CH_3$, 30H), 1.77 (pent, J = 6.9 Hz, $ArOCH_2\mathit{CH_2}(CH_2)_{15}CH_3$, 2H), 2.97 (s, $Ar(CH_2SO_2\mathit{CH_3})_2$, 6H), 3.96 (t, J = 6.4 Hz, $ArO\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3}$, 2H), 5.19 (s, J = 4.6 Hz, $Ar(\mathit{CH_2}SO_2CH_3)_2$, 4H), 6.94 (s, Ar*H*, 2H), 7.00 (s, Ar*H*, 2H).

1-(Octadecyloxy)-3,5-bis(thiocyanatomethyl)benzene (4d)

[0098] A mixture of dimesylate **4c** (2.00 g, 3.55 mmol) and KSCN (3.45 g, 35.53 mmol) in a mixture of ethanol (15 mL) and DMF (15 mL) was stirred at 140 °C for 24 h under argon. The mixture was poured into cold water to precipitate the dithiocyanate crude product **4d**. The crude product was washed several times with H_2O and purified by column chromatography on silica gel eluting with CH_2Cl_2 to obtain **4d** (1.35 g, 2.76 mmol, 78%). ^{1}H NMR (400 MHZ, $CDCl_3$): δ 0.87 (t, J = 6.9 Hz, $ArOCH_2CH_2(CH_2)_{15}\mathit{CH_3}$, 3H), 1.25-1.45 (m, $ArOCH_2CH_2\mathit{(CH_2)_{15}}CH_3$, 30H), 1.78 (pent, J = 6.9 Hz, $ArOCH_2\mathit{CH_2}(CH_2)_{15}CH_3$, 2H), 3.97 (t, J = 6.4 Hz, $ArO\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3}$, 2H), 4.10 (s, $Ar(\mathit{CH_2}SCN)_2$, 6H), 6.94 (s, Ar*H*, 2H), 7.00 (s, Ar*H*, 2H).

(5-(Octadecyloxy)-1,3-phenylene)dimethanethiol (R1ArmDT)

[0099] A solution of **4d** (1.00 g, 2.05 mmol) in THF (20 mL) was added dropwise to a suspension of $LiAlH_4$ (0.19 g, 5.12 mmol) in THF (15mL) under argon. The reaction was stirred at rt for 6 h, then quenched with H_2O, and acidified with 2 M HCl. The mixture was extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were washed with brine (1×100 mL) and water (1×100 mL), dried over $MgSO_4$, and evaporated to dryness to give **R1ArmDT** (0.83 g, 1.89 mmol, 92%). ^{1}H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, *J* = 6.9 Hz, $ArOCH_2CH_2(CH_2)_{15}\mathit{CH_3}$, 3H), 1.25-1.45 (m, $ArOCH_2CH_2\mathit{(CH_2)_{15}}CH_3$ and $Ar(CH_2\mathit{SH})2$, 32H), 1.76 (pent, *J* = 6.9 Hz, $ArOCH_2\mathit{CH_2}(CH_2)_{15}CH_3$, 2H), 3.68 (d, *J* = 7.5 Hz, $Ar(\mathit{CH_2}SH)_2$, 4H), 3.94 (t, *J* = 6.3 Hz, $ArO\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3}$, 2H), 6.74 (s, Ar*H*, 2H), 6.84 (s, Ar*H*, 2H). ^{13}CNMR (125 MHZ, $CDCl_3$): d 14.22, 22.78, 26.15, 29.01, 29.36, 29.46, 29.79, 32.02, 68.13, 112.98, 119.88, 142.99, 159.72.

S4. Synthesis of R1ArTT

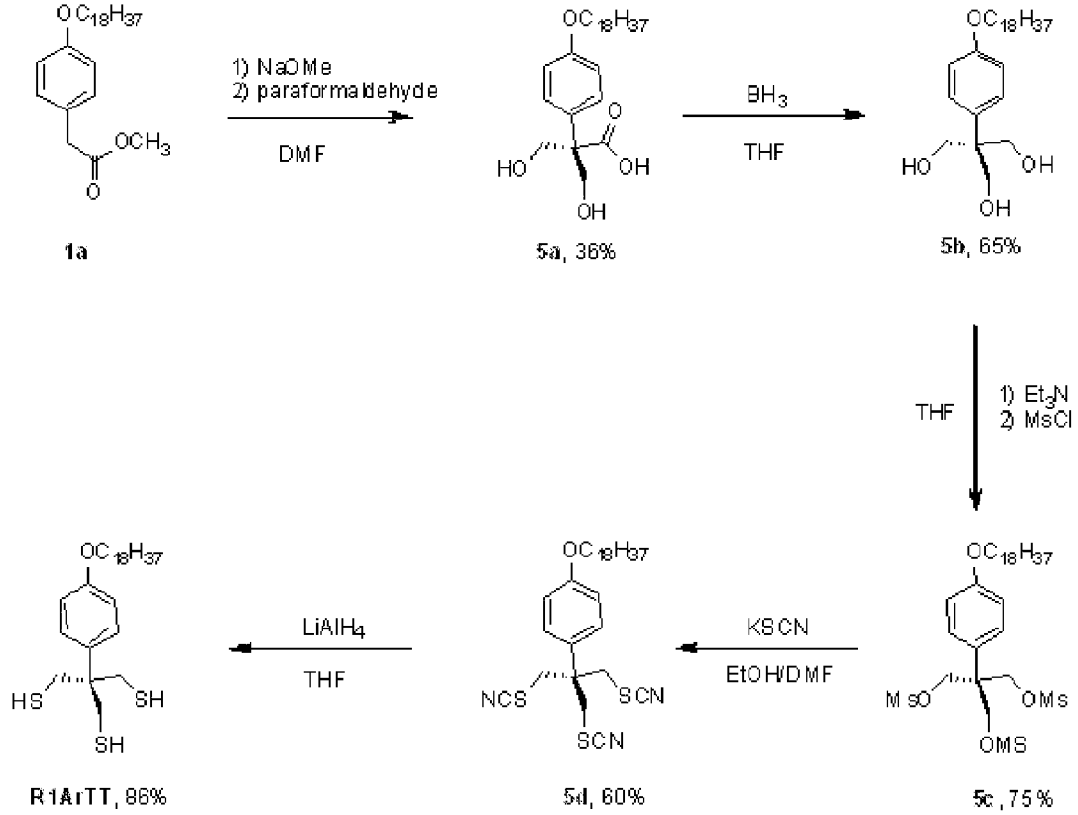
[00100] The synthetic pathway used to prepare the aromatic tridentate adsorbate, 2-(mercaptomethyl)-2-(4-(octadecyloxy)phenyl)propane-1,3-dithiol (**R1ArTT**) is shown in **Scheme S5.**

3-Hydroxy-2-(hydroxymethyl)-2-(4-(octadecyloxy)phenyl)propanoic acid (5a)

Sodium methoxide (5.5 g, 0.10 mol) and paraformadehyde (10.0 g, 0.26 mol) were added to a stirred solution of **1a** (5.00 g, 12.8 mmol) in DMF (100 mL). The mixture was stirred at rt for 120 h, then poured into a mixture of ice-water, and acidified to pH ~1 with 2 M HCl. The mixture was extracted with diethyl ether (3200 mL). The combined organic layers were washed with brine (1×100) and water (1×100 mL), dried over $MgSO_4$, and concentrated to dryness to obtain the crude product **5c**. The crude product was tritulated several times with CH_2Cl_2 and hexane to give the pure product **5a** (2.13 g, 4.59 mmol, 36%) as a white powder. ^{1}H NMR (500 MHZ, Acetone-*d6*): δ 0.91 (t, *J* = 7.4 Hz, $ArOCH_2CH_2(CH_2)_{15}\mathit{CH_3}$, 3H), 1.26-1.45 (m, $ArOCH_2CH_2\mathit{(CH_2)_{15}}CH_3$, 30H), 1.73 (pent, *J* = 6.9 Hz, $ArOCH_2\mathit{CH_2}(CH_2)_{15}CH_3$, 2H), 3.94 (t, *J* = 6.9 Hz, $ArO\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3}$, 2H), 4.11-4.26 (dd, *J* = 45.8, 10.3 Hz, $ArC\mathit{(CH_2}OH)_2$, 4H), 6.85 (d, *J* = 8.7 Hz, Ar*H*, 2H), 7.25 (d, *J* = 8.7 Hz, Ar*H*, 2H).

<u>**SCHEME S5**</u>

Synthesis Pathway of R1ArTT



2-(Hydroxymethyl)-2-(4-(octadecyloxy)phenyl)propane-1,3-diol (5b)

[00101] 1 M BH_3 (43.07 ml, 43.07 mmol) was added dropwise to a solution of **5a** (4.00 g, 8.61 mmol) in dry THF (50 mL). The mixture was stirred for 2 hours at 0°C and warmed to room temperature for overnight. The reaction was quenched with water (100 mL) and extracted with diethyl ether (3×150 mL). The combined organic layers were washed subsequently with brine (1×100 mL) and water (1×100 mL), dried over $MgSO_4$ and concentrated to dryness to obtain the crude product. The crude product was recrystallized in EtOAC to obtain triol **5b** (2.53 g, 5.62 mmol, 65%) as a white powder. ^1H NMR (500 MHZ, Acetone-*d6*): δ 0.85 (t, $J = 6.9$ Hz, $ArOCH_2CH_2(CH_2)_{15}\mathit{CH_3}$, 3H), 1.26-1.48 (m, $ArOCH_2CH_2\mathit{(CH_2)_{15}}CH_3$, 30H), 1.73 (pent, $J = 6.9$ Hz, $ArOCH_2\mathit{CH_2}(CH_2)_{15}CH_3$, 2H), 2.79 (d, $J = 17.2$, $ArC\mathit{(CH_2}OH)_3$, 3H), 3.94 (s, $ArO\mathit{CH_2}CH_2(CH_2)_{15}CH_3$, 6H), 6.81 (d, $J = 9.2$ Hz, Ar*H*, 2H), 7.34 (d, $J = 9.2$ Hz, Ar*H*, 2H).

2-(Methanesulonyl-methyl)-2-(4-(octadecyloxy)phenyl)propane-1,3-dimethanesulfonate (5c)

[0102] To the stirred solution of **5b** (2.00 g, 4.44 mmol) and triethylamine (5.57 mL, 40.0 mmol) in dry THF (25 mL) was added dropwise methansulfonyl chloride (3.10 mL, 40.0 mmol) over 5 min. Stirring of the mixture was continued at rt for 4 h under argon. The mixture of ice-cold water was poured into the reaction flask to destroy any remaining methansulfonyl chloride. The mixture was extracted with diethyl ether (3 ×150 mL). The combined organic phases were washed with 2 M HCl (1×100 mL) and water (1×100 mL), dried over MgSO$_4$, and concentrated to dryness to obtain the crude of trimesylate **5c**. Further purification by co-solvent recrytallization with CH$_2$Cl$_2$ and MeOH afforded the pure product **5c** (2.27 g, 3.31 mmol, 75%) as a white powder. ^{1}H NMR (500 MHZ, CDCl$_3$): δ 0.87 (t, *J* = 6.9 Hz, ArOCH$_2$CH$_2$(CH$_2$)$_{15}$*CH$_3$*, 3H), 1.25-1.45 (m, ArOCH$_2$CH$_2$*(CH$_2$)$_{15}$*CH$_3$, 30H), 1.77 (pent, *J* = 6.9 Hz, ArOCH$_2$*CH$_2$*(CH$_2$)$_{15}$CH$_3$, 2H), 2.98 (s, ArC(CH$_2$)$_3$(SO$_2$*CH$_3$*)$_3$, 9H), 3.94 (t, *J* = 6.9 Hz, ArO*CH$_2$*CH$_2$(CH$_2$)$_{15}$*CH$_3$*, 2H), 4.54 (s, ArC*(CH$_2$)$_3$*(SO$_2$CH$_3$)$_3$, 6H), 6.92 (d, *J* = 9.2 Hz, Ar*H*, 2H), 7.23 (d, *J* = 9.2 Hz, Ar*H*, 2H).

1-(1,3-Dithiocyanato-2-(thiocyanatomethyl)propan-2-yl)-4(octadeclyoxy)benzene (5d)

[0103] A mixture of trimesylate **5c** (2.00 g, 2.92 mmol) and KSCN (8.51 g, 87.6 mmol) in a solution of EtOH (15 mL) and DMF (15 mL) was stirred at 140 °C for 24 h. The resulting brownish solution was poured into cold water. The precipitate formed was filtrated, wash with water, and then dissolved in CH$_2$Cl$_2$. The organic layer was washed with water (1×100 mL) and brine (1×100 mL), dried over MgSO$_4$, and concentrated to dryness. The crude product was purified by column chromatography on silica gel eluting with a mixture of CH$_2$Cl$_2$:hexane (3:2) to afford **5d** (1.00 g, 1.74 mmol, 60%). ^{1}H NMR (400 MHZ, CDCl$_3$): δ 0.87 (t, *J* = 6.3 Hz, ArOCH$_2$CH$_2$(CH$_2$)$_{15}$*CH$_3$*, 3H), 1.22-1.43 (m, ArOCH$_2$CH$_2$*(CH$_2$)$_{15}$*CH$_3$, 30H), 1.75 (pent, *J* = 6.9 Hz, ArOCH$_2$*CH$_2$*(CH$_2$)$_{15}$CH$_3$, 2H), 3.68 (s, Ar(*CH$_2$*SCN)$_3$, 6H), 3.95 (t, *J* = 6.3 Hz, ArO*CH$_2$*CH$_2$(CH$_2$)$_{15}$CH$_3$, 2H), 6.96 (d, *J* = 8.0 Hz, Ar*H*, 2H), 7.12 (d, *J* = 8.0 Hz, Ar*H*, 2H).

2-(Mercaptomethyl)-2-(4-(octadecyloxy)phenyl)propane-1,3-dithiol (R1ArTT)

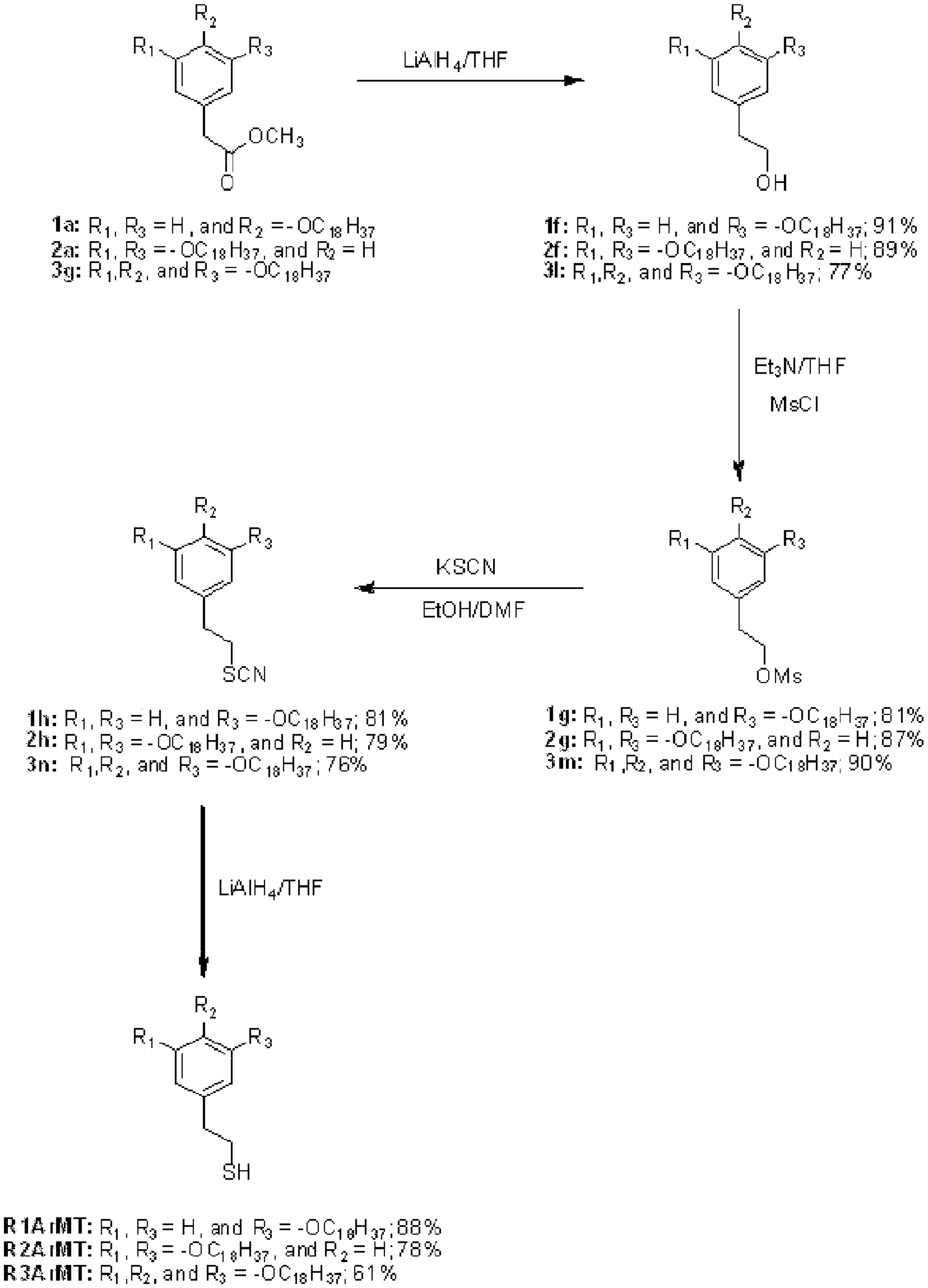
[0104] To a suspension of LiAlH$_4$ (0.10 g, 2.6 mmol) in THF (25 mL) was add dropwise a solution of **5d** (0.20 g, 0.35 mmol) in THF. The reaction was stirred at rt for 6 h, and then quenched under argon with distilled water (25 mL), and acidified with conc. HCl. After stirred for 10 min, the mixture was extracted with CH$_2$Cl$_2$ (3×100 mL). The combined organic layers were washed with brine (1×50 mL) and water (1×50 mL), dried over MgSO$_4$, and evaporated to dryness to give the crude product. The crude product was purified by column chromatography on silica gel eluting with a mixture of CH$_2$Cl$_2$ and hexame (3:2) to afford **R1ArTT** (0.15 g, 0.30 mmol, 86%). ^{1}H NMR (500 MHZ, CDCl$_3$): δ 0.88 (t, *J* = 8.7 Hz, ArOCH$_2$CH$_2$(CH$_2$)$_{15}$*CH$_3$*, 3H), 1.02 (t, *J* = 8.6 Hz, Ar(CH$_2$*SH*)$_3$, 3H), 1.24-1.48 (m, ArOCH$_2$CH$_2$*(CH$_2$)$_{15}$*CH$_3$, 30H), 1.76 (pent, *J* = 8.7 Hz, ArOCH$_2$*CH$_2$*(CH$_2$)$_{15}$CH$_3$, 2H), 3.05 (d, *J* = 8.6 Hz, Ar(CH$_2$*SH*)$_3$, 6H), 3.94 (t, *J* = 8.3 Hz, ArO*CH$_2$*CH$_2$(CH$_2$)$_{15}$CH$_3$, 2H), 6.89 (d, *J* = 8.6 Hz, Ar*H*, 2H), 7.14 (d, *J* = 8.6 Hz, Ar*H*,2H). ^{13}C NMR (125 MHZ, CDCl$_3$): d 14.23, 22.79, 26.17, 29.46, 29.70, 31.03, 32.02, 47.48, 68.05, 114.68, 128.09, 132.21, 158.13.

S5. Synthesis of the Aromatic Monodentate Thiols, R1ArMT, R2ArMT, and R3ArMT

[0105] The synthetic pathway and procedure for synthesis of **R1ArMT**, **R2ArMT**, and **R3ArMT** is illustrated in **Scheme 6.** The intermediate compounds **1a**, **2a**, and **3g** are used to prepare **R1ArMT**, **R2ArMT**, and **R3ArMT**, respectively.

SCHEME 6

Synthetic pathway of R1ArMT, R2ArMT, and R3ArMT



1a: R_1, R_3 = H, and R_2 = $-OC_{18}H_{37}$
2a: R_1, R_3 = $-OC_{18}H_{37}$, and R_2 = H
3g: R_1,R_2, and R_3 = $-OC_{18}H_{37}$

1f: R_1, R_3 = H, and R_3 = $-OC_{18}H_{37}$; 91%
2f: R_1, R_3 = $-OC_{18}H_{37}$, and R_2 = H; 89%
3l: R_1,R_2, and R_3 = $-OC_{18}H_{37}$; 77%

1h: R_1, R_3 = H, and R_3 = $-OC_{18}H_{37}$; 81%
2h: R_1, R_3 = $-OC_{18}H_{37}$, and R_2 = H; 79%
3n: R_1,R_2, and R_3 = $-OC_{18}H_{37}$; 76%

1g: R_1, R_3 = H, and R_3 = $-OC_{18}H_{37}$; 81%
2g: R_1, R_3 = $-OC_{18}H_{37}$, and R_2 = H; 87%
3m: R_1,R_2, and R_3 = $-OC_{18}H_{37}$; 90%

R1ArMT: R_1, R_3 = H, and R_3 = $-OC_{18}H_{37}$; 88%
R2ArMT: R_1, R_3 = $-OC_{18}H_{37}$, and R_2 = H; 78%
R3ArMT: R_1,R_2, and R_3 = $-OC_{18}H_{37}$; 61%

2-(4-(Octadecyloxy)phenyl)ethanol (1f)

[0106] To a suspension of $LiAlH_4$ (0.45 g, 12 mmol) in THF (25 mL) was added dropwise a solution of **1a** (2.00 g, 4.78 mmol) in THF (20 mL). The mixture was refluxed for 6 h under argon, quenched with water, and acidified with 2 M HCl. After being stirred for 10 min, the resultant mixture was extracted with CH_2Cl_2 (3×150 mL). The combined organic layers were washed subsequently with brine (3×50 mL) and water (3×50 mL), dried over $MgSO_4$, and evaporated to dryness to give (1.70 g, 4.35 mmol, 91%) of **1c**. ^1H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, *J* = 6.9 Hz, $ArOCH_2CH_2(CH_2)_{15}\mathit{CH_3}$,3H), 1.25-1.47 (m, $ArOCH_2CH_2\mathit{(CH_2)_{15}}CH_3$, 30H), 1.76 (pent, *J* = 7.4 Hz, $ArOCH_2\mathit{CH_2}(CH_2)_{15}CH_3$, 2H), 2.80 (t, *J* = 6.9 Hz, $Ar\mathit{CH_2}CH_2OH$), 3.64 (t, *J* = 6.9 Hz, $ArCH_2CH_2\mathit{OH}$, 2H), 3.81 (t, *J* = 6.9 Hz, $ArCH_2\mathit{CH_2}OH$), 1H), 3.92 (t, *J* = 7.4 Hz, $ArO\mathit{CH_2}CH_2(CH_2)_{15}CH_3$, 2H), 6.84 (d, *J* = 8.6 Hz, Ar*H*, 2H), 7.12 (d, *J* = 8.6 Hz, Ar*H*, 2H).

4-(Octadecyloxy)phenethylmethanesulfonate (1g)

[0107] To a stirred solution of **1f** (2.00 g, 4.75 mmol) and triethylamine (1.99 ml, 14.3 mmol) in anhydrous THF (25 mL) was added dropwise methansulfonyl chloride (1.11 mL, 14.3 mmol) over 5 min. Stirring of the mixture was continued at rt for 4 h under argon. Ice-cold water was poured into the reaction flask to destroy any remaining methanesulfonyl chloride. The mixture was extracted with diethyl ether (3×100 mL). The combined organic phase were washed successively with 2 M HCl (1×100 mL) and water (1×100 mL), dried over $MgSO_4$, and concentrated to dryness. A minimum volume of CH_2Cl_2 was used to dissolve the crude product, and then MeOH was added to the solution to obtain the crude mesylate **1g** (1.80 g, 3.84 mmol, 81%). The crude product was used in the next step without any purification. ^1H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, *J* = 6.9 Hz, $ArOCH_2CH_2(CH_2)_{15}\mathit{CH_3}$,3H), 1.25-1.47 (m, $ArOCH_2CH_2\mathit{(CH_2)_{15}}CH_3$, 30H), 1.76 (pent, *J* = 7.8 Hz, $ArOCH_2\mathit{CH_2}(CH_2)_{15}CH_3$, 2H), 2.84 (s, $ArCH_2CH_2SO_2\mathit{CH_3}$, 3H), 2.98 (t, *J* = 6.9 Hz, $Ar\mathit{CH_2}CH_2SO_2CH_3$, 2H), 3.92 (t, *J* = 6.9 Hz, $ArO\mathit{CH_2}CH_2(CH_2)_{15}CH_3$, 2H), 4.37 (t, *J* = 6.9 Hz, $ArCH_2\mathit{CH_2}SO_2CH_3$, 2H), 6.83 (d, *J* = 8.7 Hz, Ar*H*, 2H), 7.12 (d, *J* = 8.7 Hz, Ar*H*, 2H).

1-(Octadecyloxy)-4-(2-thiocyanatethyl)benzene (1h)

[0108] A mixture of **1g** (1.00 g, 2.13 mmol) and KSCN (2.07 g, 21.3 mmol) in the mixture of EtOH (10 mL) and DMF (10 mL) was stirred at 140°C for 24 h. The resulting mixture was poured into cold water. The precipitate formed was filtered, washed with water, and then dissolved in CH_2Cl_2 (250 mL). The organic layer was washed with saturated brine (1×50 mL), dried over $MgSO_4$, and concentrated to dryness. The crude product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to afford **1e** (0.75 g, 1.7 mmol, 81%). ^1H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, *J* = 6.9 Hz, $ArOCH_2CH_2(CH_2)_{15}\mathit{CH_3}$, 3H), 1.20-1.48 (m, $ArOCH_2CH_2\mathit{(CH_2)_{15}}CH_3$, 30H), 1.76 (pent, *J* = 6.9 Hz, $ArOCH_2\mathit{CH_2}(CH_2)_{15}CH_3$, 2H), 3.05 (t, *J* = 7.4 Hz, $Ar\mathit{CH_2}CH_2SCN$), 3.13 (t, *J* = 7.4 Hz, ArCH$_2$*CH*$_2$SCN, 2H), 3.92 (t, *J* = 6.9 Hz, ArO*CH*$_2$CH$_2$(CH$_2$)$_{15}$CH$_3$, 2H), 6.84 (d, *J* = 8.6 Hz, Ar*H*, 2H), 7.10 (d, *J* = 8.6 Hz, Ar*H*, 2H).

2-(4-Octadecyloxy)phenyl)etanethiol (R1ArMT)

[0109] To a suspension LiAlH$_4$ (0.22 g, 5.8 mmol) in THF (25 mL) was added dropwise a solution of **1e** (1.00 g, 2.31 mmol) in THF (20 mL). The reaction was stirred at rt for 6 h under argon and then quenched with water and acidified to pH ~1 by carefully adding conc. HCl. The mixture was extracted with CH$_2$Cl$_2$ (3×50 mL). The combined organic layers were washed subsequently with brine (1×50 mL) and water (1×50 mL), dried over MgSO$_4$, and evaporated to dryness to give **R1ArMT** (0.83 g, 0.20 mmol, 88%). ^{1}H NMR (500 MHZ, CDCl$_3$): δ 0.87 (t, *J* = 6.8 Hz, ArOCH$_2$CH$_2$(CH$_2$)$_{15}$*CH*$_3$,3H), 1.21-1.50 (m, ArOCH$_2$CH$_2$*(CH*$_2$*)*$_{15}$CH$_3$, and ArCH$_2$CH$_2$*SH*, 31H), 1.75 (pent, *J* = 6.8 Hz, ArOCH$_2$*CH*$_2$(CH$_2$)$_{15}$CH$_3$, 2H), 2.74 (m, ArCH$_2$*CH*$_2$SH), 2.83 (t, *J* = 7.4 Hz, Ar*CH*$_2$CH$_2$SH, 2H), 3.92 (t, *J* = 6.9 Hz, ArO*CH*$_2$CH$_2$(CH$_2$)$_{15}$CH$_3$, 2H), 6.83 (d, *J* = 8.6 Hz, Ar*H*, 2H), 7.09 (d, *J* = 8.6 Hz, Ar*H*, 2H). ^{13}CNMR (125 MHZ, CDCl$_3$): δ 14.22, 22.78, 26.14, 26.44, 29.45, 29.78, 32.01, 39.46, 68.10, 114.56, 129.66, 131.76, 157.93.

2-(3,5-Bis(octadecyloxy)phenyl)ethanol (2f)

[0110] Following the procedure described for **1f**, a solution of **2a** (2.00 g, 2.91 mmol) in THF (15 mL) was added to a suspension of LiAlH$_4$ (0.28 g, 7.2 mmol) in THF (10 mL) to obtain **2f** (1.70 g, 2.58 mmol, 89%). ^{1}H NMR (300 MHZ, CDCl$_3$): δ 0.88 (t, *J* = 6.3 Hz, Ar(OCH$_2$CH$_2$(CH$_2$)$_{15}$*CH*$_3$)$_2$, 6H), 1.24-1.43 (m, Ar(OCH$_2$CH$_2$*(CH*$_2$*)*$_{15}$CH$_3$)$_2$, 60H), 1.76 (pent, *J* = 6.3 Hz, Ar(OCH$_2$*CH*$_2$(CH$_2$)$_{15}$CH$_3$)$_2$, 4H), 2.79 (t, *J* = 6.3 Hz Ar*CH*$_2$CH$_2$OH, 2H), 3.83-3.890 (m, ArCH$_2$*CH*$_2$OH, and ArCH$_3$CH$_2$*OH*, 3H), 3.91 (t, *J* = 6.6 Hz, Ar(O*CH*$_2$CH$_2$(CH$_2$)$_{15}$*CH*$_3$)$_2$, 4H), 6.35 (s, Ar*H*, 1H), 6.36 (s, Ar*H*, 2H).

3,5-Bis(octadecyloxy)phenethylmethanesulfonate (2g)

[0111] Following the procedure described for **1g**, a mixture of **2f** (2.00 g, 3.03 mmol) and triethylamine (1.27 mL, 9.10 mmol) in THF (30 mL) was treated with methansulfonyl chloride (0.71 mL, 9.1 mmol) to obtain the crude mesylate **2g** (1.94 g, 2.65 mmol, 87%) as a white powder. ^{1}H NMR (300 MHZ, CDCl$_3$): δ 0.88 (t, *J* = 6.3 Hz, Ar(OCH$_2$CH$_2$(CH$_2$)$_{15}$*CH*$_3$)$_2$, 6H), 1.20-1.42 (m, Ar(OCH$_2$CH$_2$*(CH*$_2$*)*$_{15}$CH$_3$)$_2$, 60H), 1.76 (pent, *J* = 6.6 Hz, Ar(OCH$_2$*CH*$_2$(CH$_2$)$_{15}$CH$_3$)$_2$, 4H), 2.88 (s, ArCH$_2$CH$_2$SO$_2$*CH*$_3$, 3H), 2.97 (t, *J* = 6.6 Hz, Ar*CH*$_2$CH$_2$ SO$_2$CH$_3$, 2H), 3.91 (t, *J* = 6.6 Hz, ArO*CH*$_2$CH$_2$(CH$_2$)$_{15}$CH$_3$, 2H), 4.40 (t, *J* = 6.6 Hz, ArCH$_2$*CH*$_2$SO$_2$CH$_3$, 2H), 6.63 (s (br), Ar*H*, 3H).

1,3-Bis(octadecyloxy)-5-(2-thiocyanatoethyl)benzene (2h)

[0112] Following the procedure described for **1h**, **2g** (2.00 g, 2.73 mmol) was treated with KSCN

(2.66 g, 27.3 mmol) dissolved in a mixture of EtOH (10 mL) and DMF (10 mL). The crude product was purified by column chromatography using CH_2Cl_2:hexane (3:2) as the eluent to afford **2e** (1.52 g, 2.17 mmol, 79%). ^{1}H NMR (500 MHZ, $CDCl_3$): δ 0.88 (t, *J* = 6.9 Hz, Ar($OCH_2CH_2(CH_2)_{15}CH_3)_2$, 6H), 1.21-1.49 (m, Ar($OCH_2CH_2(\mathit{CH_2})_{15}CH_3)_2$, 60H), 1.77 (pent, *J* = 6.9 Hz, Ar($OCH_2\mathit{CH_2}(CH_2)_{15}CH_3)_2$, 4H), 3.02 (t, *J* = 6.9 Hz, Ar$\mathit{CH_2}CH_2$SCN, 2H), 3.16 (t, *J* = 6.8 Hz, Ar$CH_2\mathit{CH_2}$SCN, 2H), 3.92 (t, *J* = 6.9 Hz, Ar($O\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3})_2$, 4H), 6.32 (s, Ar*H*, 2H), 6.34 (s, Ar*H*, 1H).

2-(3,3-Bis(octadecyloxy)phenyl)ethanethiol (R2ArMT)

[0113] Following the procedure described for **R1ArMT**, a solution of **2h** (2.00 g, 2.91 mmol) in THF (15 mL) was added dropwise to a suspension of $LiAlH_4$ (0.28 g, 7.2 mmol) in THF (10 mL) to give **R2ArMT** (0.75 g, 1.1 mmol, 78%). ^{1}H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, *J* = 6.9 Hz, Ar($OCH_2CH_2(CH_2)_{15}CH_3)_2$, 6H), 1.21-1.50 (m, Ar($OCH_2CH_2(\mathit{CH_2})_{15}CH_3)_2$, and Ar$CH_2CH_2\mathit{SH}$, 61H), 1.75 (pent, *J* = 6.9 Hz, Ar($OCH_2\mathit{CH_2}(CH_2)_{15}CH_3)_2$, 4H), 2.76 (m, Ar$CH_2\mathit{CH_2}$SH, 2H), 2.83 (t, *J* = 6.9 Hz, Ar$\mathit{CH_2}CH_2$SH, 2H), 3.90 (t, *J* = 6.9 Hz, Ar($O\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3})_2$, 4H), 6.32 (s, Ar*H*, 3H). ^{13}CNMR (125 MHZ, $CDCl_3$): d 14.22, 22.79, 25.94, 26.15, 29.59, 29.70, 29.78, 32.02, 40.67, 68.08, 99.34, 107.22, 142.01, 160.46.

2-(3,4,5-Tris(octadecyloxy)phenyl)ethanol (3l)

[0114] Following the procedure described for **1f**, a solution of **3g** (2.00 g, 2.09 mmol) in THF (15 mL) was added dropwise to a suspension of $LiAlH_4$ (0.20 g, 5.2 mmol) in THF (10 mL) to give **3h** (1.70 g, 1.83 mmol, 88%). ^{1}H NMR (400 MHZ, $CDCl_3$): δ 0.87 (t, *J* = 7.4 Hz, Ar($OCH_2CH_2(CH_2)_{15}\mathit{CH_3})_3$, 9H), 1.25-1.45 (m, Ar($OCH_2CH_2(\mathit{CH_2})_{15}CH_3)_3$, 90H), 1.65-1.87 (m, Ar($OCH_2\mathit{CH_2}(CH_2)_{15}CH_3)_3$, 6H), 2.76 (t, *J* = 8.0 Hz, Ar$\mathit{CH_2}CH_2$OH, 2H), 3.85 (m, Ar$CH_2CH_2\mathit{OH}$, 1H), 3.92-3.96 (m, Ar($O\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3})_3$ and Ar$CH_2\mathit{CH_2}$OH, 8H), 6.37 (s, Ar*H*, 2H).

3,4,5-Tris(octadecyloxy)phenylmethanesulfonate (3m)

[0115] Following the procedure described for **1g**, a mixture of **3l** (1.50 g, 1.62 mmol) and triethylamine (0.68 mL, 4.8 mmol) in THF (30 mL) was treated with methanesulfonyl chloride (0.38 mL, 4.8 mmol) to obtain the crude mesylate **3l**. The crude product was dissolved in a minimum volume of CH_2Cl_2, and MeOH was added to precipitate **3l** (1.38 g, 1.37 mmol, 85%) as a white powder. ^{1}H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, *J* = 7.4 Hz, Ar($OCH_2CH_2(CH_2)_{15}\mathit{CH_3})_3$, 9H), 1.20-1.48 (m, Ar($OCH_2CH_2(\mathit{CH_2})_{15}CH_3)_3$, 90H), 1.69-1.80 (m, Ar($OCH_2\mathit{CH_2}(CH_2)_{15}CH_3)_3$, 6H), 2.85 (s, Ar$CH_2CH_2SO_2\mathit{CH_3}$, 3H), 2.95 (t, *J* = 7.4 Hz, Ar$\mathit{CH_2}CH_2SO_2CH_3$, 2H), 3.90-3.96 (m, Ar($O\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3})_3$, 6H), 4.38 (t, *J* = 7.4 Hz, Ar$CH_2\mathit{CH_2}SO_2CH_3$, 2H), 6.37 (s, Ar*H*, 2H).

1,2,3-Tris(octadecyloxy(-5-(2-thiocyanatoethyl)benzene (3n)

[0116] Following the procedure described for **1h**, **3m** (2.00 g, 1.99 mmol) was treated with KSCN (1.93 g, 19.9 mmol) dissolved in a mixture of EtOH (10 mL) and DMF (10 mL). The crude product was purified by column chromatography using CH_2Cl_2:hexane (3:2) as the eluent to afford **3n** (1.50 g, 1.54 mmol, 78%). ^{1}H NMR (400 MHZ, $CDCl_3$): δ 0.87 (t, $J = 6.9$ Hz, $Ar(OCH_2CH_2(CH_2)_{15}\mathit{CH_3})_3$, 9H), 1.24-1.49 (m, $Ar(OCH_2CH_2\mathit{(CH_2)_{15}}CH_3)_3$, 90H), 1.75-1.81 (m, $Ar(OCH_2\mathit{CH_2}(CH_2)_{15}CH_3)_3$, 6H), 3.06 (t, $J = 7.4$ Hz, $Ar\mathit{CH_2}CH_2SCN$, 2H), 3.14 (t, $J = 7.4$ Hz, $ArCH_2\mathit{CH_2}SCN$, 2H), 3.92 (m, $Ar(O\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3})_3$, 6H), 6.37 (s, $Ar\mathit{H}$, 2H).

2-(3,4,5-Tris(octadecyloxy)phenyl)ethanethiol (R3ArMT)

[0117] Following the procedure described for **R1ArMT**, a solution of **3n** (1.00 g, 1.03 mmol) in THF (15 mL) was added dropwise to a suspension of $LiAlH_4$ (0.10 g, 2.6 mmol) in THF (10 mL) to give the crude product. Purification was performed by column chromatography with CH_2Cl_2:hexane (3:2) as the eluent to afford pure **R3ArMT** (0.67 g, 0.71 mmol, 69%) as a white powder. ^{1}H NMR (500 MHZ, $CDCl_3$): δ 0.87 (t, $J = 6.9$ Hz, $Ar(OCH_2CH_2(CH_2)_{15}\mathit{CH_3})_3$, 9H), 1.25-1.49 (m, $Ar(OCH_2CH_2\mathit{(CH_2)_{15}}CH_3)_3$ and $ArCH_2CH_2\mathit{SH}$, 91H), 1.75-1.81 (m, $Ar(OCH_2\mathit{CH_2}(CH_2)_{15}CH_3)_3$, 6H), 2.76 (m, $ArCH_2\mathit{CH_2}SH$, 2H), 2.80 (t, $J = 6.9$ Hz, $Ar\mathit{CH_2}CH_2SCN$, 2H), 3.90 (m, $Ar(O\mathit{CH_2}CH_2(CH_2)_{15}\mathit{CH_3})_3$, 6H), 6.36 (s, $Ar\mathit{H}$, 2H). ^{13}CNMR (500 MHZ, $CDCl_3$): 14.22, 22.79, 26.21, 26.24, 29.47, 29.54, 29.75, 29.81, 30.43, 32.02, 40.70, 62.23,73.51, 107.25, 135.00, 136.92, 153.17.

PREPARATION OF SAMs

Materials and Methods

[0118] Gold shot (99.99%) was purchased from Americana Precious Metals. Chromium rods (99.9%) were purchased from R. D. Mathis Company. Polished single-crystal Si(100) wafers were purchased from Silicon Inc. and rinsed with absolute ethanol (Aaper Alcohol and Chemical Co.) before use. The contacting liquids used for wettability measurements were the highest purity available from Aldrich Chemical Co. and were used without further purification. The starting material, and chemicals used in the syntheses of all adsorbates were mostly purchased from Aldrich Chemical Co. Solvents used in the syntheses were distilled over calcium hydride and stored under argon. Column chromatography was performed using silica gel (40-64 mm) and thin-layer chromatography (TLC) was carried out using 200 mm-thick silica gel plates, which were purchased from Sorbent Technologies. Inc. Nuclear Magnetic Resonance (NMR) spectra were recorded on JOEL ECX-400 and ECA-500 spectrometers operating at 400 MHZ and 500 MHZ, respectively. The data were obtained in $CDCl_3$ and referenced to δ 7.26 and 77.00 ppm for ^1H NMR and ^{13}C NMR, respectively.

Preparation of SAMs

[0119] Under a vacuum, ~ 10^{-5} Torr, a thin layer (100 Å) of chromium was first evaporated onto polished silicon (100) wafers to assist the adhesion of gold on the silicon substrate. Subsequently, the deposition of 1000 Å of gold onto the chromium-coated silicon wafers was performed. The resultant wafers were rinsed with absolute ethanol and blown dry with ultra-pure nitrogen before use. The freshly prepared gold-coated wafers were cut into slides (1×4 cm) and the slides were cleaned by rinsing with absolute ethanol and blown dry with ultra-pure nitrogen before collecting the optical constants of the substrates by ellipsometry. The glass vials used to store each thiol solution were previously cleaned with piranha solution (3:1 mixture of H_2SO_4/H_2O_2) and rinsed thoroughly with deionized water, followed by absolute ethanol. [*Caution: Piranha solution is highly corrosive, should never be stored, and should be handled with extreme care.*] The slides were then immersed in the appropriate 1 mM thiol solution and allowed to equilibrate for 72 hours at room temperature. Samples were rinsed with toluene, THF, methanol, and then ethanol, successively, and dried with a flow of ultra-pure nitrogen before characterization.

Characterization of SAMs

Ellipsometric Measurements

[0120] A Rudolph Research Auto EL III ellipsometer equipped with a He-Ne laser (632.8 nm) at angle of incidence of 70° was utilized to measure the film thicknesses. An approximate value of film refractive index of 1.45 was applied for all measurements. For each sample, optical constants were determined from six measurements from two separate slides using three different spots for each slide. Reported values of thicknesses were the average of the measurements over the experimental collections.

Contact Angle Measurements

[0121] Contact angles for the SAMs were measured on a Ramé-Hart model 100 contact angle goniometer. The contacting liquid water (H_2O) , hexadecane (HD), and decalin (DEC) were dispensed (advancing angle, q_a) and withdrawn (receding angle, q_r) on the surfaces using a Matrix Technologies micro-Electrapette 25 at the slowest speed (1 mL/s). The contact angles were carried out at room temperature while keeping the pipet tip in contact with the drop. Contact angle values were reported by averaging the results from six independent drops from two separate slides with three drops per slide, including measurements for both drop edges.

X-ray Photoelectron Spectroscopy (XPS)

[0122] XPS spectra were recorded with a PHI 5700 X-ray photoelectron spectrometer equipped with a monochromatic Al Ka X-ray source (hn = 1486.7 eV) incident at 90° relative to the axis of the hemispherical energy analyzer. Spectra were taken at high resolution with a pass energy of 23.5 eV, a photoelectron taken off angle of 45° from the surface, and an analyzer spot diameter of 2.0 mm. The pressure in the chamber during the measurements was $\sim 4\times 10^{-8}$ Torr. The binding energies were referenced to the Au $4f_{7/2}$ peak at 84.0 eV.

Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS)

[0123] IR spectra were collected with a Nicolet NEXUS 670 Fourier transform IR spectrometer equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector and a Hinds Instrument PEM-90 photoelastic modulator. All measurements were performed in a sample compartment purged with nitrogen gas during the course of the experiments. The spectra were collected at 2 cm^{-1} spectral resolution for 512 scans with a grazing angle for the infrared beam aligned at 80°.

Thermal Desorption of SAMs at the Elevated Temperature

[0124] Thermal stability experiments were performed in isooctane at 80±2 °C. SAM-coated gold slides were immersed into the stirred solvent and periodically removed at systematic intervals of time. The samples were subsequently rinsed with toluene, THF, methanol, and ethanol, in that order, and blown dry in a stream of ultra-pure nitrogen. The samples were immediately characterized by ellipsometry and then reimmersed in the heating solvent.

[0125] While the invention described herein specifically focuses on methods for the preparation of stable homogeneously mixed thin film coatings through the use of tailored aromatic-based adsorbates, one of ordinary skills in the art, with the benefit of this disclosure, would recognize the extension of such approach to other systems.

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[0127] All references cited herein are incorporated by reference. Although the invention has been disclosed with reference to its preferred embodiments, from reading this description those of skill in the art may appreciate changes and modification that may be made which do not depart from the scope and spirit of the invention as described above and claimed hereafter.

CLAIMS

We claim:

1. A method for preparing homogeneously self-assembled monolayers (SAMs) comprising:

adsorbing a mono-dentate absorbate, a bi-dentate absorbate, a tri-dentate absorbate or a mixture or combination thereof onto a surface of a substrate to form a SAM modified surface,

where the adsorbates comprise an aromatic ring including one dentate head group or a plurality of dentate head groups and one tunable tail group or a plurality of tunable tail groups, and

where the SAM exhibit: (1) homogenous lateral chain distributions, (2) no or substantially no phase separation or islanding across SAM modified surfaces, and (3) enhanced stability as compared to a corresponding linear alkyl thiol monodentate adsorbate.

2. The method of claim 1, wherein the surface comprises a metal surface.

3. The method of claim 1, wherein the absorbate or mixture thereof comprise one monodentate adsorbate or a mixture of monodentate absorbates.

4. The method of claim 1, wherein the absorbate or mixture thereof comprise one bidentate adsorbate or a mixture of bidentate absorbates.

5. The method of claim 4, wherein the bidentate adsorbate or the mixture of bidentate absorbates comprise a non-symmetrical spiroalkanedithiol or a mixture of non-symmetrical spiroalkanedithiols.

6. The method of claim 1, wherein the absorbate or mixture thereof comprise one tridentate adsorbate or a mixture of tridentate absorbates.

6. The method of claim 1, wherein the absorbate or mixture thereof comprise compounds of the general formulas (I-V):

$$\mathbf{Z^1,Z^2,Z^3\text{–}A(SH)_k(RSH)_l(CH_{m1}(SH)_{m2})_n} \qquad \text{(I)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R^{a1}}$, halogenated carbyl group $\mathbf{R^{a2}}$, a fluorinated carbyl group $\mathbf{R^{a3}}$, a per-fluorinated carbyl group $\mathbf{R^{a4}}$, an alkoxy group $\mathbf{OR^b}$ group, an amine group $\mathbf{NR^cR^d}$, an amido group $\mathbf{C(O)NR^eR^f}$, an amido group $\mathbf{NR^xC(O)R^y}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, or $\mathbf{Z^3}$ groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the $\mathbf{R^{a1}}$ and the $\mathbf{R^{c,e,y}}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR^g}$ groups, $\mathbf{C(O)NR^hR^i}$ groups, or $\mathbf{NR^wC(O)R^z}$ groups, (5) the $\mathbf{R^{a2\text{-}a4}}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the $\mathbf{R^{d,f,x}}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, (7) $\mathbf{R^{g,h,i,w,z}}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms, (8) **k**, **l**, **m1**, **m2** and **n** are integers, (9) **k** has a value between 1 and 3, when **l** and **n** have a value of 0, (10) **l** has a value between 1 and 3, when **k** and **n** have a value of 0, (11) **n** has a value of 1, when **k** and **l** have a value of 0, and (12) **m1** + **m2** is equal to 3. In certain embodiments, at least two of $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are not hydrogen atoms. In other embodiments, all of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are not hydrogen atoms;

$$\mathbf{Z^1,Z^2,Z^3\text{-}ACH_{m1}(SH)_{m2}} \qquad \text{(II)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R^{a1}}$, halogenated carbyl group $\mathbf{R^{a2}}$, a fluorinated carbyl group $\mathbf{R^{a3}}$, a per-fluorinated carbyl group $\mathbf{R^{a4}}$, an alkoxy group $\mathbf{OR^b}$ group, an amine group $\mathbf{NR^cR^d}$, an amido group $\mathbf{C(O)NR^eR^f}$, an amido group $\mathbf{NR^xC(O)R^y}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, or $\mathbf{Z^3}$ groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the $\mathbf{R^{a1}}$ and the $\mathbf{R^{c,e,y}}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR^g}$ groups, $\mathbf{C(O)NR^hR^i}$ groups, or $\mathbf{NR^wC(O)R^z}$ groups, (5) the $\mathbf{R^{a2\text{-}a4}}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the $\mathbf{R^{d,f,x}}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, (7) $\mathbf{R^{g,h,i,w,z}}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms, (8) **m1** and **m2** are integers, and (9) **m1** + **m2** is equal to 3;

$$\mathbf{Z^1,Z^2,Z^3\text{-}A\text{-}m\text{-}(RSH)_2} \qquad \text{(III)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R}^{a1}$, halogenated carbyl group $\mathbf{R}^{a2}$, a fluorinated carbyl group $\mathbf{R}^{a3}$, a per-fluorinated carbyl group $\mathbf{R}^{a4}$, an alkoxy group $\mathbf{OR}^{b}$ group, an amine group $\mathbf{NR}^{c}\mathbf{R}^{d}$, an amido group $\mathbf{C(O)NR}^{e}\mathbf{R}^{f}$, an amido group $\mathbf{NR}^{x}\mathbf{C(O)R}^{y}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z}^1$, $\mathbf{Z}^2$, or $\mathbf{Z}^3$ groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the $\mathbf{R}^{a1}$ and the $\mathbf{R}^{c,e,y}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR}^{g}$ groups, $\mathbf{C(O)NR}^{h}\mathbf{R}^{i}$ groups, or $\mathbf{NR}^{w}\mathbf{C(O)R}^{z}$ groups, (5) the $\mathbf{R}^{a2\text{-}a4}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the $\mathbf{R}^{d,f,x}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (7) $\mathbf{R}^{g,h,i,w,z}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms;

$$\mathbf{Z^1,Z^2,Z^3\text{-}Py\text{-}m\text{-}(RSH)_2} \tag{IV}$$

where: (1) **Py** is pyridine, (2) **-m-** means the two **RSH** groups meta to each other, (3) $\mathbf{Z}^1$, $\mathbf{Z}^2$, and $\mathbf{Z}^3$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R}^{a1}$, halogenated carbyl group $\mathbf{R}^{a2}$, a fluorinated carbyl group $\mathbf{R}^{a3}$, a per-fluorinated carbyl group $\mathbf{R}^{a4}$, an alkoxy group $\mathbf{OR}^{b}$ group, an amine group $\mathbf{NR}^{c}\mathbf{R}^{d}$, an amido group $\mathbf{C(O)NR}^{e}\mathbf{R}^{f}$, an amido group $\mathbf{NR}^{x}\mathbf{C(O)R}^{y}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z}^1$, $\mathbf{Z}^2$, and $\mathbf{Z}^3$ groups is not hydrogen, (4) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (5) the $\mathbf{R}^{a1}$ and the $\mathbf{R}^{c,e,y}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR}^{g}$ groups, $\mathbf{C(O)NR}^{h}\mathbf{R}^{i}$ groups, or $\mathbf{NR}^{w}\mathbf{C(O)R}^{z}$ groups, (6) the $\mathbf{R}^{a2\text{-}a4}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (7) the $\mathbf{R}^{d,f,x}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (8) $\mathbf{R}^{g,h,i,w,z}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms; and

$$\mathbf{Z^1,Z^2\text{-}Cp\text{-}m\text{-}(RSH)_2} \tag{V}$$

where: (1) **Cp** is 5-member aromatic ring, where one of the carbon atoms of the **Cp** ring may be replaced by an oxygen atom, a nitrogen atom, or a sulfur atom, (2) **-m-** means that the two **RSH** groups are meta to each other or occupy the 2 and 5 positions of the five membered **Cp** ring, (3) $\mathbf{Z}^1$ and $\mathbf{Z}^2$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R}^{a1}$, halogenated carbyl group $\mathbf{R}^{a2}$, a fluorinated carbyl group $\mathbf{R}^{a3}$, a per-fluorinated carbyl group $\mathbf{R}^{a4}$, an alkoxy group $\mathbf{OR^b}$ group, an amine group $\mathbf{NR^cR^d}$, an amido group $\mathbf{C(O)NR^eR^f}$, an amido group $\mathbf{NR^xC(O)R^y}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z^1}$ and $\mathbf{Z^2}$ groups is not a hydrogen atom, (4) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (5) the $\mathbf{R^{a1}}$ and the $\mathbf{R^{c,e,y}}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR^g}$ groups, $\mathbf{C(O)NR^hR^i}$ groups, or $\mathbf{NR^wC(O)R^z}$ groups, (6) the $\mathbf{R^{a2\text{-}a4}}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (7) the $\mathbf{R^{d,f,x}}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (8) $\mathbf{R^{g,h,i,w,z}}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms.

7. The method of claim 1, wherein the absorbate or mixture thereof comprise compounds of the general formula (I):

$$\mathbf{Z^1,Z^2,Z^3\text{-}A(SH)_k(RSH)_l(CH_{m1}(SH)_{m2})_n} \qquad \text{(I)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R^{a1}}$, halogenated carbyl group $\mathbf{R^{a2}}$, a fluorinated carbyl group $\mathbf{R^{a3}}$, a per-fluorinated carbyl group $\mathbf{R^{a4}}$, an alkoxy group $\mathbf{OR^b}$ group, an amine group $\mathbf{NR^cR^d}$, an amido group $\mathbf{C(O)NR^eR^f}$, an amido group $\mathbf{NR^xC(O)R^y}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, or $\mathbf{Z^3}$ groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the $\mathbf{R^{a1}}$ and the $\mathbf{R^{c,e,y}}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR^g}$ groups, $\mathbf{C(O)NR^hR^i}$ groups, or $\mathbf{NR^wC(O)R^z}$ groups, (5) the $\mathbf{R^{a2\text{-}a4}}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the $\mathbf{R^{d,f,x}}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, (7) $\mathbf{R^{g,h,i,w,z}}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms, (8) **k**, **l**, **m1**, **m2** and **n** are integers, (9) **k** has a value between 1 and 3, when **l** and **n** have a value of 0, (10) **l** has a value between 1 and 3, when **k** and **n** have a value of 0, (11) **n** has a value of 1, when **k** and **l** have a value of 0, and (12) **m1** + **m2** is equal to 3. In certain embodiments, at least two of $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are not hydrogen atoms. In other embodiments, all of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are not hydrogen atoms.

8. The method of claim 1, wherein the absorbate or mixture thereof comprise compounds of the general formula (II):

$$\mathbf{Z^1,Z^2,Z^3\text{-}ACH_{m1}(SH)_{m2}} \qquad \text{(II)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) **Z^1**, **Z^2**, and **Z^3** groups are the same or different and comprise a hydrogen atom, a carbyl group **R^{a1}**, halogenated carbyl group **R^{a2}**, a fluorinated carbyl group **R^{a3}**, a per-fluorinated carbyl group **R^{a4}**, an alkoxy group **OR^b** group, an amine group **NR^cR^d**, an amido group **$C(O)NR^eR^f$**, an amido group **$NR^xC(O)R^y$**, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the **Z^1**, **Z^2**, or **Z^3** groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the **R^{a1}** and the **$R^{c,e,y}$** groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, **NR^g** groups, **$C(O)NR^hR^i$** groups, or **$NR^wC(O)R^z$** groups, (5) the **$R^{a2\text{-}a4}$** may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the **$R^{d,f,x}$** groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, (7) **$R^{g,h,i,w,z}$** are linear or branched carbyl groups having between 1 and 10 carbon atoms, (8) **m1** and **m2** are integers, and (9) **m1** + **m2** is equal to 3.

9. The method of claim 1, wherein the absorbate or mixture thereof comprise compounds of the general formula (III):

$$\mathbf{Z^1,Z^2,Z^3\text{-}A\text{-}m\text{-}(RSH)_2} \qquad \text{(III)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) **Z^1**, **Z^2**, and **Z^3** groups are the same or different and comprise a hydrogen atom, a carbyl group **R^{a1}**, halogenated carbyl group **R^{a2}**, a fluorinated carbyl group **R^{a3}**, a per-fluorinated carbyl group **R^{a4}**, an alkoxy group **OR^b** group, an amine group **NR^cR^d**, an amido group **$C(O)NR^eR^f$**, an amido group **$NR^xC(O)R^y$**, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the **Z^1**, **Z^2**, or **Z^3** groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the **R^{a1}** and the **$R^{c,e,y}$** groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, **NR^g** groups, **$C(O)NR^hR^i$** groups, or

$NR^wC(O)R^z$ groups, (5) the **$R^{a2\text{-}a4}$** may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the **$R^{d,f,x}$** groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (7) **$R^{g,h,i,w,z}$** are linear or branched carbyl groups having between 1 and 10 carbon atoms.

10. The method of claim 1, wherein the absorbate or mixture thereof comprise compounds of the general formula (IV):

$$Z^1,Z^2,Z^3\text{-}Py\text{-}m\text{-}(RSH)_2 \qquad \text{(IV)}$$

where: (1) **Py** is pyridine, (2) **-m-** means the two **RSH** groups meta to each other, (3) **Z^1**, **Z^2**, and **Z^3** groups are the same or different and comprise a hydrogen atom, a carbyl group **R^{a1}**, halogenated carbyl group **R^{a2}**, a fluorinated carbyl group **R^{a3}**, a per-fluorinated carbyl group **R^{a4}**, an alkoxy group **OR^b** group, an amine group **NR^cR^d**, an amido group **$C(O)NR^eR^f$**, an amido group **$NR^xC(O)R^y$**, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the **Z^1**, **Z^2**, and **Z^3** groups is not hydrogen, (4) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (5) the **R^{a1}** and the **$R^{c,e,y}$** groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, **NR^g** groups, **$C(O)NR^hR^i$** groups, or **$NR^wC(O)R^z$** groups, (6) the **$R^{a2\text{-}a4}$** may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (7) the **$R^{d,f,x}$** groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (8) **$R^{g,h,i,w,z}$** are linear or branched carbyl groups having between 1 and 10 carbon atoms.

11. The method of claim 1, wherein the absorbate or mixture thereof comprise compounds of the general formula (V):

$$Z^1,Z^2\text{-}Cp\text{-}m\text{-}(RSH)_2 \qquad \text{(V)}$$

where: (1) **Cp** is 5-member aromatic ring, where one of the carbon atoms of the **Cp** ring may be replaced by an oxygen atom, a nitrogen atom, or a sulfur atom, (2) **-m-** means that the two **RSH** groups are meta to each other or occupy the 2 and 5 positions of the five membered **Cp** ring, (3) **Z^1** and **Z^2** groups are the same or different and comprise a hydrogen atom, a carbyl group **R^{a1}**, halogenated carbyl group **R^{a2}**, a fluorinated carbyl group **R^{a3}**, a per-fluorinated carbyl group **R^{a4}**, an alkoxy group **OR^b** group, an amine group **NR^cR^d**, an amido group **$C(O)NR^eR^f$**, an amido group **$NR^xC(O)R^y$**, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z}^1$ and $\mathbf{Z}^2$ groups is not a hydrogen atom, (4) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (5) the $\mathbf{R}^{a1}$ and the $\mathbf{R}^{c,e,y}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR}^g$ groups, $\mathbf{C(O)NR}^h\mathbf{R}^i$ groups, or $\mathbf{NR}^w\mathbf{C(O)R}^z$ groups, (6) the $\mathbf{R}^{a2\text{-}a4}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (7) the $\mathbf{R}^{d,f,x}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (8) $\mathbf{R}^{g,h,i,w,z}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms.

12. A self-assembled monolayer composition comprising an absorbate or mixture thereof comprise compounds of the general formulas (I-V):

$$\mathbf{Z^1,Z^2,Z^3\text{–}A(SH)_k(RSH)_l(CH_{m1}(SH)_{m2})_n} \qquad \text{(I)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) $\mathbf{Z}^1$, $\mathbf{Z}^2$, and $\mathbf{Z}^3$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R}^{a1}$, halogenated carbyl group $\mathbf{R}^{a2}$, a fluorinated carbyl group $\mathbf{R}^{a3}$, a per-fluorinated carbyl group $\mathbf{R}^{a4}$, an alkoxy group $\mathbf{OR}^b$ group, an amine group $\mathbf{NR}^c\mathbf{R}^d$, an amido group $\mathbf{C(O)NR}^e\mathbf{R}^f$, an amido group $\mathbf{NR}^x\mathbf{C(O)R}^y$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z}^1$, $\mathbf{Z}^2$, or $\mathbf{Z}^3$ groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the $\mathbf{R}^{a1}$ and the $\mathbf{R}^{c,e,y}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR}^g$ groups, $\mathbf{C(O)NR}^h\mathbf{R}^i$ groups, or $\mathbf{NR}^w\mathbf{C(O)R}^z$ groups, (5) the $\mathbf{R}^{a2\text{-}a4}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the $\mathbf{R}^{d,f,x}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, (7) $\mathbf{R}^{g,h,i,w,z}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms, (8) **k**, **l**, **m1**, **m2** and **n** are integers, (9) **k** has a value between 1 and 3, when **l** and **n** have a value of 0, (10) **l** has a value between 1 and 3, when **k** and **n** have a value of 0, (11) **n** has a value of 1, when **k** and **l** have a value of 0, and (12) **m1** + **m2** is equal to 3. In certain embodiments, at least two of $\mathbf{Z}^1$, $\mathbf{Z}^2$, and $\mathbf{Z}^3$ groups are not hydrogen atoms. In other embodiments, all of the $\mathbf{Z}^1$, $\mathbf{Z}^2$, and $\mathbf{Z}^3$ groups are not hydrogen atoms;

$$\mathbf{Z^1,Z^2,Z^3\text{-}ACH_{m1}(SH)_{m2}} \qquad \text{(II)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R^{a1}}$, halogenated carbyl group $\mathbf{R^{a2}}$, a fluorinated carbyl group $\mathbf{R^{a3}}$, a per-fluorinated carbyl group $\mathbf{R^{a4}}$, an alkoxy group $\mathbf{OR^b}$ group, an amine group $\mathbf{NR^cR^d}$, an amido group $\mathbf{C(O)NR^eR^f}$, an amido group $\mathbf{NR^xC(O)R^y}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, or $\mathbf{Z^3}$ groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the $\mathbf{R^{a1}}$ and the $\mathbf{R^{c,e,y}}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR^g}$ groups, $\mathbf{C(O)NR^hR^i}$ groups, or $\mathbf{NR^wC(O)R^z}$ groups, (5) the $\mathbf{R^{a2\text{-}a4}}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the $\mathbf{R^{d,f,x}}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, (7) $\mathbf{R^{g,h,i,w,z}}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms, (8) **m1** and **m2** are integers, and (9) **m1** + **m2** is equal to 3;

$$\mathbf{Z^1,Z^2,Z^3\text{-}A\text{-}m\text{-}(RSH)_2} \qquad \text{(III)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R^{a1}}$, halogenated carbyl group $\mathbf{R^{a2}}$, a fluorinated carbyl group $\mathbf{R^{a3}}$, a per-fluorinated carbyl group $\mathbf{R^{a4}}$, an alkoxy group $\mathbf{OR^b}$ group, an amine group $\mathbf{NR^cR^d}$, an amido group $\mathbf{C(O)NR^eR^f}$, an amido group $\mathbf{NR^xC(O)R^y}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, or $\mathbf{Z^3}$ groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the $\mathbf{R^{a1}}$ and the $\mathbf{R^{c,e,y}}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR^g}$ groups, $\mathbf{C(O)NR^hR^i}$ groups, or $\mathbf{NR^wC(O)R^z}$ groups, (5) the $\mathbf{R^{a2\text{-}a4}}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the $\mathbf{R^{d,f,x}}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (7) $\mathbf{R^{g,h,i,w,z}}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms;

$$\mathbf{Z^1,Z^2,Z^3\text{-}Py\text{-}m\text{-}(RSH)_2} \qquad \text{(IV)}$$

where: (1) **Py** is pyridine, (2) -**m**- means the two **RSH** groups meta to each other, (3) $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R^{a1}}$, halogenated carbyl group $\mathbf{R^{a2}}$, a fluorinated carbyl group $\mathbf{R^{a3}}$, a per-fluorinated carbyl group $\mathbf{R^{a4}}$, an alkoxy group

$\mathbf{OR^b}$ group, an amine group $\mathbf{NR^cR^d}$, an amido group $\mathbf{C(O)NR^eR^f}$, an amido group $\mathbf{NR^xC(O)R^y}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups is not hydrogen, (4) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (5) the $\mathbf{R^{a1}}$ and the $\mathbf{R^{c,e,y}}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR^g}$ groups, $\mathbf{C(O)NR^hR^i}$ groups, or $\mathbf{NR^wC(O)R^z}$ groups, (6) the $\mathbf{R^{a2\text{-}a4}}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (7) the $\mathbf{R^{d,f,x}}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (8) $\mathbf{R^{g,h,i,w,z}}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms; and

$$\mathbf{Z^1,Z^2\text{-}Cp\text{-}m\text{-}(RSH)_2} \tag{V}$$

where: (1) **Cp** is 5-member aromatic ring, where one of the carbon atoms of the **Cp** ring may be replaced by an oxygen atom, a nitrogen atom, or a sulfur atom, (2) **-m-** means that the two **RSH** groups are meta to each other or occupy the 2 and 5 positions of the five membered **Cp** ring, (3) $\mathbf{Z^1}$ and $\mathbf{Z^2}$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R^{a1}}$, halogenated carbyl group $\mathbf{R^{a2}}$, a fluorinated carbyl group $\mathbf{R^{a3}}$, a per-fluorinated carbyl group $\mathbf{R^{a4}}$, an alkoxy group $\mathbf{OR^b}$ group, an amine group $\mathbf{NR^cR^d}$, an amido group $\mathbf{C(O)NR^eR^f}$, an amido group $\mathbf{NR^xC(O)R^y}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z^1}$ and $\mathbf{Z^2}$ groups is not a hydrogen atom, (4) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (5) the $\mathbf{R^{a1}}$ and the $\mathbf{R^{c,e,y}}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR^g}$ groups, $\mathbf{C(O)NR^hR^i}$ groups, or $\mathbf{NR^wC(O)R^z}$ groups, (6) the $\mathbf{R^{a2\text{-}a4}}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (7) the $\mathbf{R^{d,f,x}}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (8) $\mathbf{R^{g,h,i,w,z}}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms.

13. The composition of claim 12, wherein the absorbate or mixture thereof comprise compounds of the general formula (I):

$$\mathbf{Z^1,Z^2,Z^3\text{-}A(SH)_k(RSH)_l(CH_{m1}(SH)_{m2})_n} \tag{I}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R}^{a1}$, halogenated carbyl group $\mathbf{R}^{a2}$, a fluorinated carbyl group $\mathbf{R}^{a3}$, a per-fluorinated carbyl group $\mathbf{R}^{a4}$, an alkoxy group $\mathbf{OR}^{b}$ group, an amine group $\mathbf{NR}^{c}\mathbf{R}^{d}$, an amido group $\mathbf{C(O)NR}^{e}\mathbf{R}^{f}$, an amido group $\mathbf{NR}^{x}\mathbf{C(O)R}^{y}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z}^1$, $\mathbf{Z}^2$, or $\mathbf{Z}^3$ groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the $\mathbf{R}^{a1}$ and the $\mathbf{R}^{c,e,y}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR}^{g}$ groups, $\mathbf{C(O)NR}^{h}\mathbf{R}^{i}$ groups, or $\mathbf{NR}^{w}\mathbf{C(O)R}^{z}$ groups, (5) the $\mathbf{R}^{a2\text{-}a4}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the $\mathbf{R}^{d,f,x}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, (7) $\mathbf{R}^{g,h,i,w,z}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms, (8) **k**, **l**, **m1**, **m2** and **n** are integers, (9) **k** has a value between 1 and 3, when **l** and **n** have a value of 0, (10) **l** has a value between 1 and 3, when **k** and **n** have a value of 0, (11) **n** has a value of 1, when **k** and **l** have a value of 0, and (12) **m1** + **m2** is equal to 3. In certain embodiments, at least two of $\mathbf{Z}^1$, $\mathbf{Z}^2$, and $\mathbf{Z}^3$ groups are not hydrogen atoms. In other embodiments, all of the $\mathbf{Z}^1$, $\mathbf{Z}^2$, and $\mathbf{Z}^3$ groups are not hydrogen atoms.

14. The composition of claim 12, wherein the absorbate or mixture thereof comprise compounds of the general formula (II):

$$\mathbf{Z}^1,\mathbf{Z}^2,\mathbf{Z}^3\text{-}\mathbf{ACH}_{m1}(\mathbf{SH})_{m2} \qquad \text{(II)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) $\mathbf{Z}^1$, $\mathbf{Z}^2$, and $\mathbf{Z}^3$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R}^{a1}$, halogenated carbyl group $\mathbf{R}^{a2}$, a fluorinated carbyl group $\mathbf{R}^{a3}$, a per-fluorinated carbyl group $\mathbf{R}^{a4}$, an alkoxy group $\mathbf{OR}^{b}$ group, an amine group $\mathbf{NR}^{c}\mathbf{R}^{d}$, an amido group $\mathbf{C(O)NR}^{e}\mathbf{R}^{f}$, an amido group $\mathbf{NR}^{x}\mathbf{C(O)R}^{y}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z}^1$, $\mathbf{Z}^2$, or $\mathbf{Z}^3$ groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the $\mathbf{R}^{a1}$ and the $\mathbf{R}^{c,e,y}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR}^{g}$ groups, $\mathbf{C(O)NR}^{h}\mathbf{R}^{i}$ groups, or $\mathbf{NR}^{w}\mathbf{C(O)R}^{z}$ groups, (5) the $\mathbf{R}^{a2\text{-}a4}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the $\mathbf{R}^{d,f,x}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, (7) $\mathbf{R}^{g,h,i,w,z}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms, (8) **m1** and **m2** are integers, and (9) **m1** + **m2** is equal to 3.

15. The composition of claim 12, wherein the absorbate or mixture thereof comprise compounds of the general formula (III):

$$\mathbf{Z^1,Z^2,Z^3\text{-}A\text{-}m\text{-}(RSH)_2} \qquad \text{(III)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) $\mathbf{Z}^1$, $\mathbf{Z}^2$, and $\mathbf{Z}^3$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R}^{a1}$, halogenated carbyl group $\mathbf{R}^{a2}$, a fluorinated carbyl group $\mathbf{R}^{a3}$, a per-fluorinated carbyl group $\mathbf{R}^{a4}$, an alkoxy group $\mathbf{OR}^b$ group, an amine group $\mathbf{NR}^c\mathbf{R}^d$, an amido group $\mathbf{C(O)NR}^e\mathbf{R}^f$, an amido group $\mathbf{NR}^x\mathbf{C(O)R}^y$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z}^1$, $\mathbf{Z}^2$, or $\mathbf{Z}^3$ groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the $\mathbf{R}^{a1}$ and the $\mathbf{R}^{c,e,y}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR}^g$ groups, $\mathbf{C(O)NR}^h\mathbf{R}^i$ groups, or $\mathbf{NR}^w\mathbf{C(O)R}^z$ groups, (5) the $\mathbf{R}^{a2\text{-}a4}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the $\mathbf{R}^{d,f,x}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (7) $\mathbf{R}^{g,h,i,w,z}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms.

16. The composition of claim 12, wherein the absorbate or mixture thereof comprise compounds of the general formula (IV):

$$\mathbf{Z^1,Z^2,Z^3\text{-}Py\text{-}m\text{-}(RSH)_2} \qquad \text{(IV)}$$

where: (1) **Py** is pyridine, (2) **-m-** means the two **RSH** groups meta to each other, (3) $\mathbf{Z}^1$, $\mathbf{Z}^2$, and $\mathbf{Z}^3$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R}^{a1}$, halogenated carbyl group $\mathbf{R}^{a2}$, a fluorinated carbyl group $\mathbf{R}^{a3}$, a per-fluorinated carbyl group $\mathbf{R}^{a4}$, an alkoxy group $\mathbf{OR}^b$ group, an amine group $\mathbf{NR}^c\mathbf{R}^d$, an amido group $\mathbf{C(O)NR}^e\mathbf{R}^f$, an amido group $\mathbf{NR}^x\mathbf{C(O)R}^y$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z}^1$, $\mathbf{Z}^2$, and $\mathbf{Z}^3$ groups is not hydrogen, (4) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (5) the $\mathbf{R}^{a1}$ and the $\mathbf{R}^{c,e,y}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, **NR**^{g} groups, **C(O)NR**^{h}**R**^{i} groups, or **NR**^{w}**C(O)R**^{z} groups, (6) the **R**$^{a2\text{-}a4}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (7) the **R**^{d,f,x} groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (8) **R**^{g,h,i,w,z} are linear or branched carbyl groups having between 1 and 10 carbon atoms.

17. The composition of claim 12, wherein the absorbate or mixture thereof comprise compounds of the general formula (V):

$$\mathbf{Z^1,Z^2\text{-}Cp\text{-}m\text{-}(RSH)_2} \qquad \text{(V)}$$

where: (1) **Cp** is 5-member aromatic ring, where one of the carbon atoms of the **Cp** ring may be replaced by an oxygen atom, a nitrogen atom, or a sulfur atom, (2) **-m-** means that the two **RSH** groups are meta to each other or occupy the 2 and 5 positions of the five membered **Cp** ring, (3) **Z**^{1} and **Z**^{2} groups are the same or different and comprise a hydrogen atom, a carbyl group **R**^{a1}, halogenated carbyl group **R**^{a2}, a fluorinated carbyl group **R**^{a3}, a per-fluorinated carbyl group **R**^{a4}, an alkoxy group **OR**^{b} group, an amine group **NR**^{c}**R**^{d}, an amido group **C(O)NR**^{e}**R**^{f}, an amido group **NR**^{x}**C(O)R**^{y}, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the **Z**^{1} and **Z**^{2} groups is not a hydrogen atom, (4) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (5) the **R**^{a1} and the **R**^{c,e,y} groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, **NR**^{g} groups, **C(O)NR**^{h}**R**^{i} groups, or **NR**^{w}**C(O)R**^{z} groups, (6) the **R**$^{a2\text{-}a4}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (7) the **R**^{d,f,x} groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (8) **R**^{g,h,i,w,z} are linear or branched carbyl groups having between 1 and 10 carbon atoms.

18. The composition of claim 12, further comprises two or more compounds of formulas (I-V).

19. A substrate composition comprising:

a surface including a self-assembled monolayer composition formed thereon, there the self-assembled monolayer composition comprises an absorbate or mixture thereof comprise compounds of the general formulas (I-V):

$$\mathbf{Z^1,Z^2,Z^3\text{–}A(SH)_k(RSH)_l(CH_{m1}(SH)_{m2})_n} \qquad \text{(I)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R^{a1}}$, halogenated carbyl group $\mathbf{R^{a2}}$, a fluorinated carbyl group $\mathbf{R^{a3}}$, a per-fluorinated carbyl group $\mathbf{R^{a4}}$, an alkoxy group $\mathbf{OR^b}$ group, an amine group $\mathbf{NR^cR^d}$, an amido group $\mathbf{C(O)NR^eR^f}$, an amido group $\mathbf{NR^xC(O)R^y}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, or $\mathbf{Z^3}$ groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the $\mathbf{R^{a1}}$ and the $\mathbf{R^{c,e,y}}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR^g}$ groups, $\mathbf{C(O)NR^hR^i}$ groups, or $\mathbf{NR^wC(O)R^z}$ groups, (5) the $\mathbf{R^{a2\text{-}a4}}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the $\mathbf{R^{d,f,x}}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, (7) $\mathbf{R^{g,h,i,w,z}}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms, (8) **k**, **l**, **m1**, **m2** and **n** are integers, (9) **k** has a value between 1 and 3, when **l** and **n** have a value of 0, (10) **l** has a value between 1 and 3, when **k** and **n** have a value of 0, (11) **n** has a value of 1, when **k** and **l** have a value of 0, and (12) **m1** + **m2** is equal to 3. In certain embodiments, at least two of $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are not hydrogen atoms. In other embodiments, all of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are not hydrogen atoms;

$$\mathbf{Z^1,Z^2,Z^3\text{-}ACH_{m1}(SH)_{m2}} \qquad \text{(II)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R^{a1}}$, halogenated carbyl group $\mathbf{R^{a2}}$, a fluorinated carbyl group $\mathbf{R^{a3}}$, a per-fluorinated carbyl group $\mathbf{R^{a4}}$, an alkoxy group $\mathbf{OR^b}$ group, an amine group $\mathbf{NR^cR^d}$, an amido group $\mathbf{C(O)NR^eR^f}$, an amido group $\mathbf{NR^xC(O)R^y}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, or $\mathbf{Z^3}$ groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the $\mathbf{R^{a1}}$ and the $\mathbf{R^{c,e,y}}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR^g}$ groups, $\mathbf{C(O)NR^hR^i}$ groups, or $\mathbf{NR^wC(O)R^z}$ groups, (5) the $\mathbf{R^{a2\text{-}a4}}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the $\mathbf{R^{d,f,x}}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, (7) $\mathbf{R^{g,h,i,w,z}}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms, (8) **m1** and **m2** are integers, and (9) **m1** + **m2** is equal to 3;

$$\mathbf{Z^1,Z^2,Z^3\text{-}A\text{-}m\text{-}(RSH)_2} \quad \text{(III)}$$

where: (1) **A** is an aromatic group, where one of the carbon atoms of the group may be replaced by an oxygen atom (O), a nitrogen atom (N), or or a sulfur atom (S), (2) $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R^{a1}}$, halogenated carbyl group $\mathbf{R^{a2}}$, a fluorinated carbyl group $\mathbf{R^{a3}}$, a per-fluorinated carbyl group $\mathbf{R^{a4}}$, an alkoxy group $\mathbf{OR^b}$ group, an amine group $\mathbf{NR^cR^d}$, an amido group $\mathbf{C(O)NR^eR^f}$, an amido group $\mathbf{NR^xC(O)R^y}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, or $\mathbf{Z^3}$ groups is not a hydrogen atom, (3) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (4) the $\mathbf{R^{a1}}$ and the $\mathbf{R^{c,e,y}}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR^g}$ groups, $\mathbf{C(O)NR^hR^i}$ groups, or $\mathbf{NR^wC(O)R^z}$ groups, (5) the $\mathbf{R^{a2\text{-}a4}}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (6) the $\mathbf{R^{d,f,x}}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (7) $\mathbf{R^{g,h,i,w,z}}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms;

$$\mathbf{Z^1,Z^2,Z^3\text{-}Py\text{-}m\text{-}(RSH)_2} \quad \text{(IV)}$$

where: (1) **Py** is pyridine, (2) **-m-** means the two **RSH** groups meta to each other, (3) $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R^{a1}}$, halogenated carbyl group $\mathbf{R^{a2}}$, a fluorinated carbyl group $\mathbf{R^{a3}}$, a per-fluorinated carbyl group $\mathbf{R^{a4}}$, an alkoxy group $\mathbf{OR^b}$ group, an amine group $\mathbf{NR^cR^d}$, an amido group $\mathbf{C(O)NR^eR^f}$, an amido group $\mathbf{NR^xC(O)R^y}$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z^1}$, $\mathbf{Z^2}$, and $\mathbf{Z^3}$ groups is not hydrogen, (4) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (5) the $\mathbf{R^{a1}}$ and the $\mathbf{R^{c,e,y}}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR^g}$ groups, $\mathbf{C(O)NR^hR^i}$ groups, or $\mathbf{NR^wC(O)R^z}$ groups, (6) the $\mathbf{R^{a2\text{-}a4}}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (7) the $\mathbf{R^{d,f,x}}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (8) $\mathbf{R^{g,h,i,w,z}}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms; and

$$\mathbf{Z^1,Z^2\text{-}Cp\text{-}m\text{-}(RSH)_2} \quad \text{(V)}$$

where: (1) **Cp** is 5-member aromatic ring, where one of the carbon atoms of the **Cp** ring may be replaced by an oxygen atom, a nitrogen atom, or a sulfur atom, (2) **-m-** means that the two **RSH** groups are meta to each other or occupy the 2 and 5 positions of the five membered **Cp** ring, (3) $\mathbf{Z}^1$ and $\mathbf{Z}^2$ groups are the same or different and comprise a hydrogen atom, a carbyl group $\mathbf{R}^{a1}$, halogenated carbyl group $\mathbf{R}^{a2}$, a fluorinated carbyl group $\mathbf{R}^{a3}$, a per-fluorinated carbyl group $\mathbf{R}^{a4}$, an alkoxy group $\mathbf{OR}^b$ group, an amine group $\mathbf{NR}^c\mathbf{R}^d$, an amido group $\mathbf{C(O)NR}^e\mathbf{R}^f$, an amido group $\mathbf{NR}^x\mathbf{C(O)R}^y$, an oligoethylene glycol (**OEG**) group, or a polyethylene glycol (**PEG**) group provided that at least one of the $\mathbf{Z}^1$ and $\mathbf{Z}^2$ groups is not a hydrogen atom, (4) **R** is the same or different carbyl groups having between 1 and 3 carbon atoms, (5) the $\mathbf{R}^{a1}$ and the $\mathbf{R}^{c,e,y}$ groups may be linear or branched carbyl groups having between about 12 to 40 carbon atoms and sufficient hydrogens atoms to satisfy valencies, where one or more carbon atoms may be replaced by oxygen atoms, $\mathbf{NR}^g$ groups, $\mathbf{C(O)NR}^h\mathbf{R}^i$ groups, or $\mathbf{NR}^w\mathbf{C(O)R}^z$ groups, (6) the $\mathbf{R}^{a2\text{-}a4}$ may be linear or branched carbyl groups having between about 12 to 40 carbon atoms, (7) the $\mathbf{R}^{d,f,x}$ groups may be hydrogen atoms or linear or branched carbyl groups having between 1 and 10 carbon atoms, and (8) $\mathbf{R}^{g,h,i,w,z}$ are linear or branched carbyl groups having between 1 and 10 carbon atoms.

20. The composition of claim 19, wherein the self-assembled monolayer composition further comprises two or more compounds of formulas (I-V).

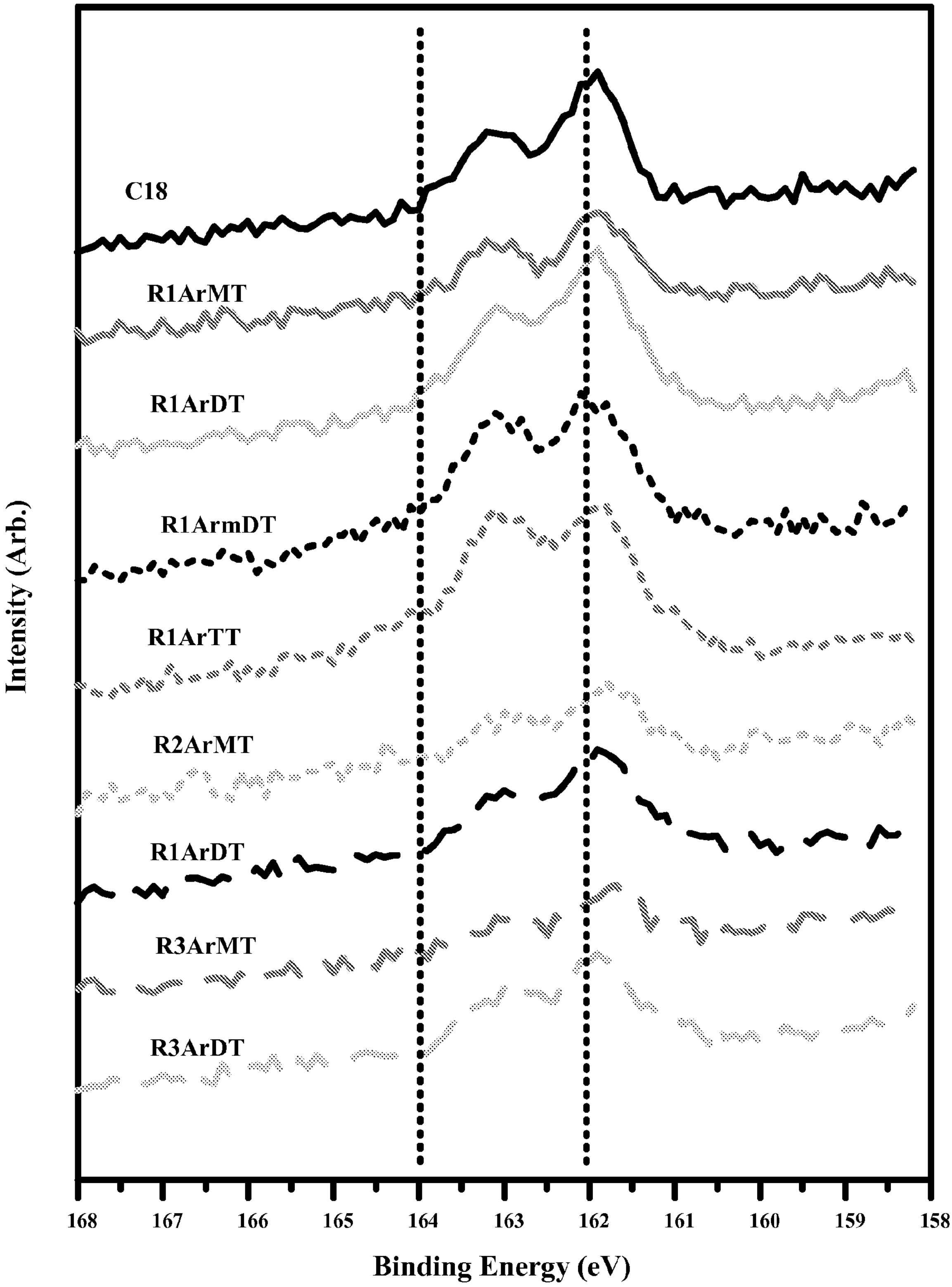
C18
R1ArMT
R1ArDT
R1ArmDT
R1ArTT
R2ArMT
R1ArDT
R3ArMT
R3ArDT
Intensity (Arb.)
168
167
166
165
164
163
162
161
160
159
158
Binding Energy (eV)

FIG. 1

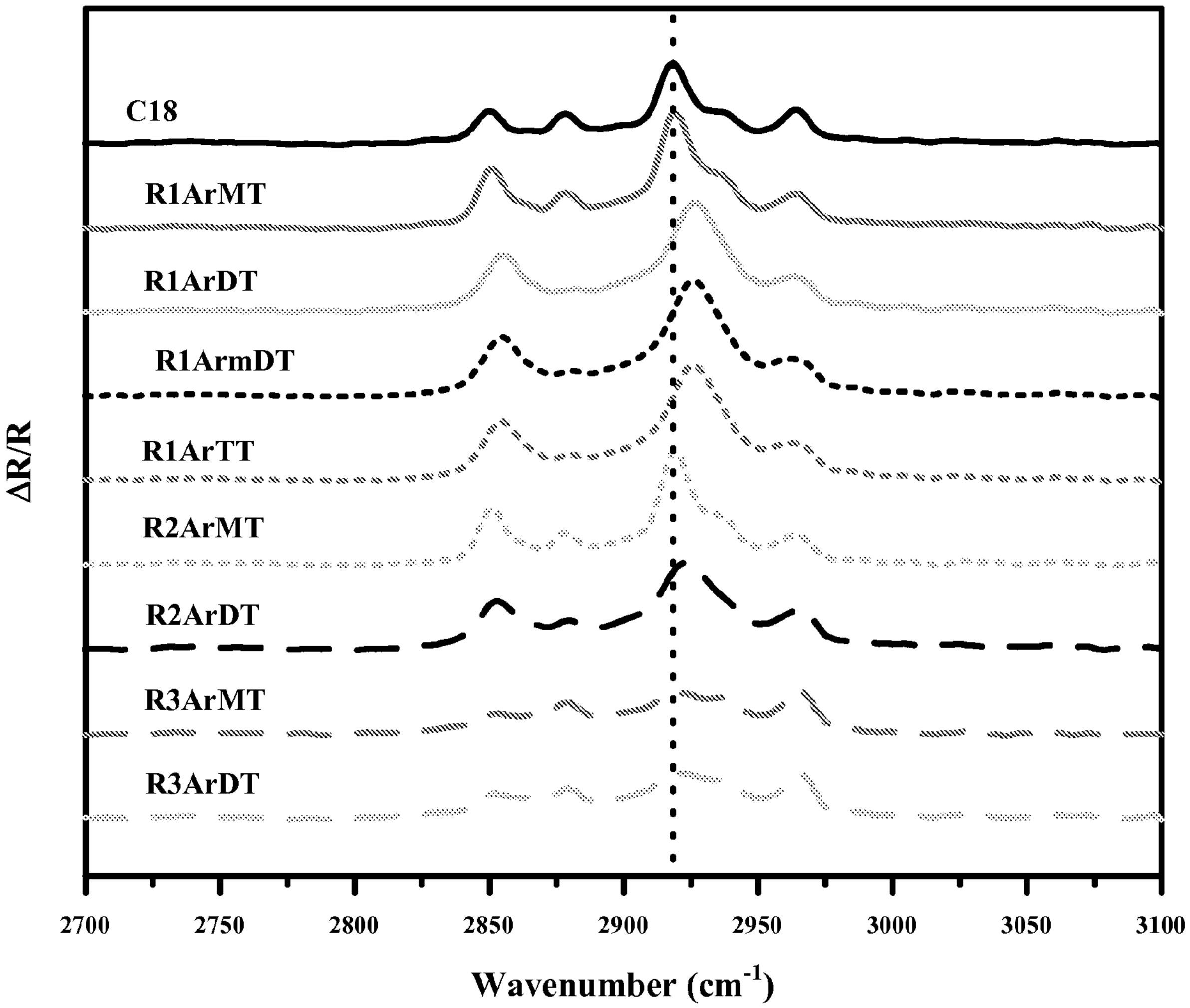
C18
R1ArMT
R1ArDT
R1ArmDT
R1ArTT
R2ArMT
R2ArDT
R3ArMT
R3ArDT
ΔR/R
2700
2750
2800
2850
2900
2950
3000
3050
3100
Wavenumber (cm^{-1})

FIG. 2

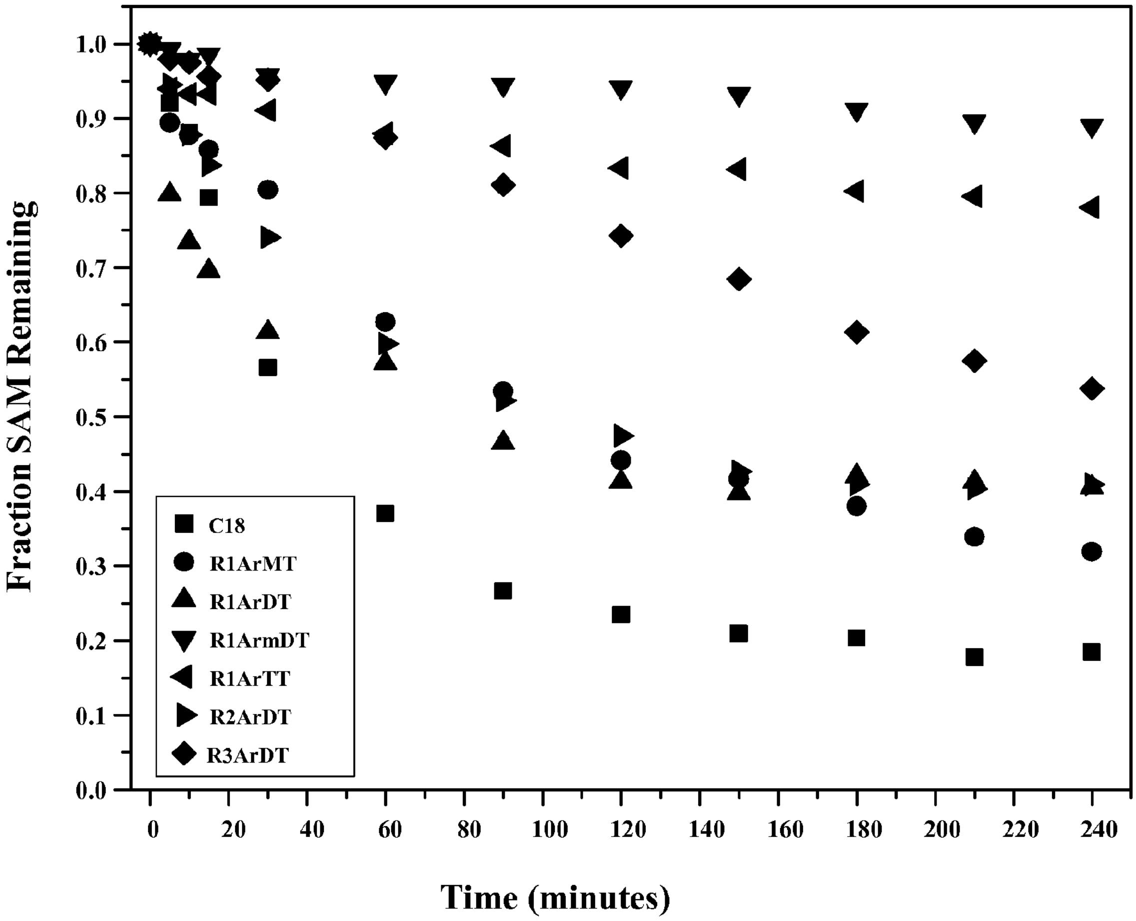
Fraction SAM Remaining
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
20
40
60
80
100
120
140
160
180
200
220
240
Time (minutes)
■ C18
● R1ArMT
▲ R1ArDT
▼ R1ArmDT
◀ R1ArTT
▶ R2ArDT
◆ R3ArDT

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/029643

A. CLASSIFICATION OF SUBJECT MATTER

B01J 20/22(2006.01)i, C07C 323/16(2006.01)i, C07C 321/10(2006.01)i, C09D 4/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J 20/22; G01N 31/22; C07K 2/00; C12Q 1/68; C07C 323/16; C07C 321/10; C09D 4/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: self-assembled monolayers, SAMs, monodentate, bidentate, tridentate, absorbate, tail group, head group, stability

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GARG, N. et al., "Self-Assembled Monolayers Based on Chelating Aromatic Dithiols on Gold", Langmuir, 18 June 1998, Vol. 14, No. 14, pages 3815-3819. See pages 3815-3816 & 3818-3819.	1,2,4
A		3,5,6
A	US 2007-0140901 A1 (BUCK, M. et al.) 21 June 2007 See abstract; claims 25, 36, 38, 39, 41-43, 45, 46.	1-6
A	SRISOMBAT, L. et al., "Preparation, Characterization, and Chemical Stability of Gold Nanoparticles Coated with Mono-, Bis-, and Tris-Chelating Alkanethiols", Langmuir, 12 July 2008, Vol. 24, No. 15, pages 7750-7754. See pages 7750, 7751, 7754.	1-6
A	HAN, S. W. et al., "Self-Assembled Monolayers of Aromatic Thiol and Selenol on Silver: Comparative Study of Adsorptivity and Stability", Langmuir, 29 September 2001, Vol. 17, No. 22, pages 6981-6987. See pages 6981-6983 & 6987.	1-6
A	US 5620850 A (BAMDAD, C. C. et al.) 15 April 1997 See abstract; claims 1, 12, 13.	1-6

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 12 July 2013 (12.07.2013)	Date of mailing of the international search report **15 July 2013 (15.07.2013)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea Facsimile No. +82-42-472-7140	Authorized officer KIM Dong Seok Telephone No. +82-42-481-8647

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 6(1), 7-20
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
The claims 6(1) & 7-20 are not considered clear because either their subject matter is not clearly defined or they refer to such claim(s). For example, the value of k, l and n cannot be clearly defined in the general formula I if the features (9)-(11) are to be fulfilled simultaneously. Similar problems exists in the general formula II-V regarding the features (2)-(7).

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/029643

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007-0140901 A1	21/06/2007	GB 0406841 D0	28/04/2004
		GB 0618673 D0	08/11/2006
		GB 2426724 A	06/12/2006
		GB 2426724 B	03/09/2008
		US 8241841 B2	14/08/2012
		WO 2005-092516 A1	06/10/2005
US 5620850 A	15/04/1997	US 2002-0042074 A1	11/04/2002
		US 2006-0040276 A1	23/02/2006
		US 6197515 B1	06/03/2001
		US 6322979 B1	27/11/2001
		US 6809196 B2	26/10/2004