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(54) Title: POLYMERS FOR THIN FILM COATINGS

(57) Abstract: The present invention provides new materials that combine the advantages of well-defined polymeric starting materials and the convenience of surface modification by physical methods into one package and, thus, offers a general and powerful platform suitable for use in numerous applications.



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Polymers for Thin Film Coatings

FIELD

[0001] The present disclosure relates to polymers for thin film coatings,
5 uses and related methods.

BACKGROUND

[0002] In this specification where a document, act or item of knowledge is referred to or discussed, this reference or discussion is not an admission that
10 the document, act or item of knowledge or any combination thereof was at the priority date, publicly available, known to the public, part of common general knowledge, or otherwise constitutes prior art under the applicable statutory provisions; or is known to be relevant to an attempt to solve any problem with which this specification is concerned.

15 **[0003]** Current technologies for surface modification with polymers use surface-bound monomers to initiate formation of polymers thereon, which leads to a polymer thin film or coating formed on the surface. There are several disadvantages associated with such a type of surface-bound monomer based polymerization, including, but not limited to, difficulties in
20 reproducibility of the surface-bound polymeric thin film structure and decreased electronic and optical properties of the surface-bound polymeric thin film.

[0004] Thus, there is a need in the art for consistently reproducible surface-bound polymeric thin film structures that do not exhibit diminished electronic
25 and optical properties.

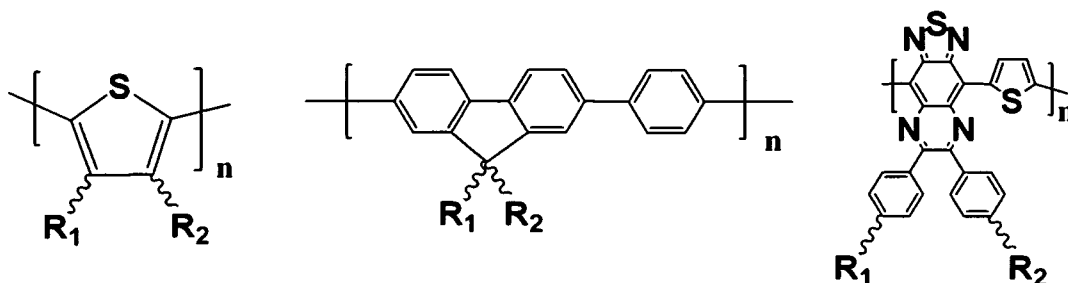
[0005] While certain aspects of conventional technologies have been discussed to facilitate disclosure of the invention, Applicants in no way disclaim these technical aspects, and it is contemplated that the claimed invention may encompass or include one or more of the conventional
30 technical aspects discussed herein.

SUMMARY

[0006] According to certain aspects, the present invention provides new materials that combine the advantages of well-defined polymeric starting materials and the convenience of surface modification by physical methods into one package and, thus, offers a general and powerful platform suitable for use in numerous applications.

[0007] According to certain aspects, the present invention provides well-defined conjugated and non-conjugated polymeric starting materials that can be formed as thin films or coatings to functionalize surfaces with chemical, biological and nano materials. Such functionalized surfaces can be used in the sensing, energy, medical and biotechnology industries. Thin films can optionally be characterized as films having a thickness on the order of about 1nm to about 1 μm .

[0008] According to one aspect, the present invention provides well-defined conjugated polymeric starting materials based on polymers of thiophene, fluorene or benzathiadiazole of the general formula shown below.



wherein:

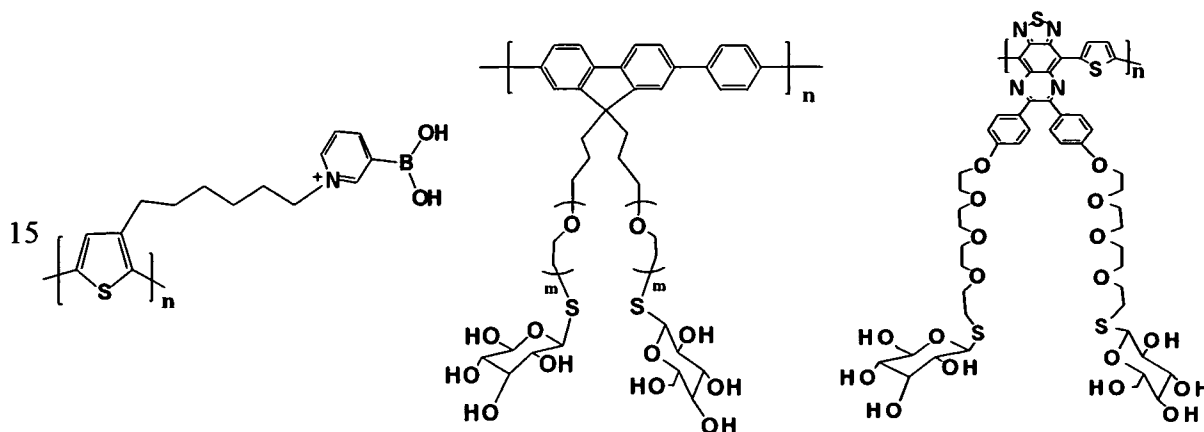
~~~~~ = oligo- or poly- ethylene glycol, an optionally substituted alkyl chain or an optionally substituted conjugated chain where the chains are optionally substituted with polyethylene glycol or polyethyleimine;

$n$  = any integer greater than 1; and

$R_1$  and/or  $R_2$  = H, alkyl, alkene, alkyne, where the number of carbon atoms are 1 to 4 in the case of alkyl, 2 to 6 in the case of alkene, and 2 to 6 in the case of alkyne, OH, Br, Cl, I, F, SH, COOH,  $\text{NH}_2$ , CHO, maleimide, NHS ester, a heterocyclic compound that can form a metal complex, a carbohydrate, a protein, a peptide, DNA, RNA, an antibody, an antigen, an

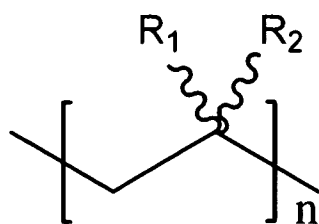
enzyme, a bacteria, a redox molecule, a host molecule, a guest molecule, a hapten, a lipid, a microbe, an aptamer, or a sugar; wherein  $R_1$  can be the same or different as  $R_2$  and wherein at least one of  $R_1$  and  $R_2$  is  $NH_2$ ,  $COOH$ ,  $OH$  or  $SH$ .

- 5 **[0009]** According to one aspect, the present invention provides well-defined conjugated polymeric starting materials based on polymers of thiophene, fluorene or benzathiadiazole that comprise water soluble side-chains comprising at least one of an alcohol, an amine and a carboxylic acid. Shown below are thiophene-, fluorene- and benzathiadiazole-based polymer
- 10 starting materials derivatized with alcohol groups.



20

**[0010]** According to another aspect, the present invention provides well-defined non-conjugated polymeric starting materials based on alkyl chain polymers of the general formula shown below.



25 wherein:

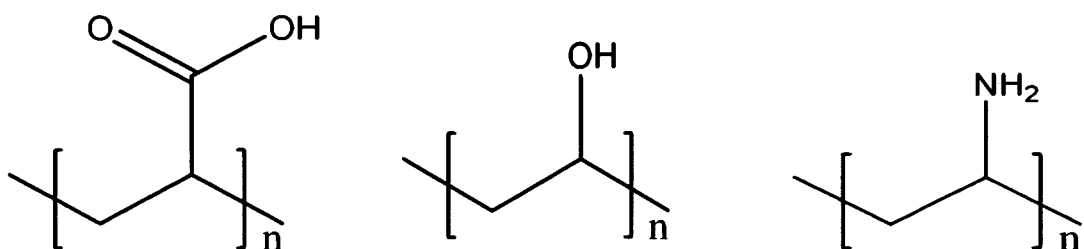
~~~~~ = oligo- or poly- ethylene glycol, an optionally substituted alkyl chain or an optionally substituted conjugated chain where the chains are optionally substituted with polyethylene glycol or polyethyleimine;

n = any integer greater than 1;

R_1 and/or R_2 = H, alkyl, alkene, alkyne, OH, Br, Cl, I, F, SH, COOH, NH₂, CHO, maleimide, NHS ester, a heterocyclic compound that can form a metal complex, other applicable functional groups, a carbohydrate, a protein, a peptide, DNA, RNA, an antibody, an antigen, an enzyme, a bacteria, a redox molecule, a host molecule, a guest molecule, a hapten, a lipid, a microbe, an aptamer, or a sugar;

wherein R_1 can be the same or different as R_2 and wherein at least one of R_1 and R_2 is NH₂, COOH, OH or SH.

- 10 **[0011]** According to another aspect, the present invention provides well-defined non-conjugated polymeric starting materials based on alkyl chain polymers that comprise water soluble side-chains comprising at least one of an alcohol, an amine and a carboxylic acid, as shown below.



- 15 **[0012]** According to a further aspect, the present invention provides surfaces modified with the aforementioned polymeric starting materials. Such surfaces are contemplated to be, without limitation, electrode surfaces, for example, carbon electrode surfaces and metallic electrode surfaces. Other surfaces contemplated can be, without limitation, semiconducting surfaces.
- 20 **[0013]** According to still another aspect, the present invention provides surfaces modified with surface-coupled redox active molecules.

- [0014]** According to yet another aspect, the present invention provides methods for modifying surfaces with the polymeric starting materials mentioned directly above. Such methods are important for developing new materials comprising modified surfaces with biological, chemical and/or nano- functionalities.
- 25

[0015] The present invention may address one or more of the problems and deficiencies of the prior art discussed above. However, it is contemplated that the invention may prove useful in addressing other problems and deficiencies, or provide benefits and advantages, in a number of technical areas. Therefore the claimed invention should not necessarily be construed as being limited to addressing any of the particular problems or deficiencies discussed herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] These and other feature of this invention will now be described with reference to the drawings of certain embodiments which are intended to illustrate and not to limit the invention.

[0017] Figure 1 shows a cyclic voltammogram of Polymer Starting Material (1), carried out in 0.1 M aqueous NaClO_4 solution.

[0018] Figure 2 shows a cyclic voltammogram of 10 mM aqueous potassium ferrocyanide solution at a glassy carbon electrode before and after formation of a thin film thereon based on Polymer Starting Material (1).

[0019] Figure 3 shows SEM images of a glassy carbon electrode before and after formation of a thin film thereon based on Polymer Starting Material (1).

Figure 3A shows the SEM image before polymer thin film formation and Figure 3B shows the SEM image after polymer thin film formation.

[0020] Figure 4 shows elemental analysis of the Polymer Starting Material (1) film on a glassy carbon electrode.

[0021] Figure 5 shows a cyclic voltammogram of Polymer Starting Material (2), carried out in 0.1 M solution NaClO_4 solution.

[0022] Figure 6 shows a cyclic voltammogram of a Polymer Starting Material (2)-caffeic acid modified surface carried out in 0.1 M solution NaClO_4 solution.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0023] Further aspects, features and advantages of this invention will become apparent from the detailed description which follows.

[0024] Well-defined polymeric starting materials for surface modification are described herein. Such polymeric starting materials in accordance with the present invention can be, for example, conjugated polymers based on thiophene, fluorene or benzothiadiazole that comprise water soluble side-chains such as an alcohol, an amine or a carboxylic acid. For example, the polymer denoted below as Polymeric Starting Material (1) is representative of a well-defined conjugated polymeric starting material in accordance with the present invention. Other such polymeric starting materials in accordance with the present invention can be, for example, non-conjugated polymers based on alkyl chain polymers that comprise water soluble side-chains comprising at least one of an alcohol, an amine and a carboxylic acid. For example, the polymer denoted below as polymeric starting material (2) is representative of a well-defined non-conjugated polymeric starting material in accordance with the present invention.

[0025] The surfaces to be modified with polymeric starting materials in accordance with the present invention are not particularly limited and can be, without limitation, a conducting surface. A representative conductive surface may be, for example, a metallic surface, such as a metallic electrode or a carbon surface, such as a carbon, or glassy carbon, electrode. Other surfaces contemplated by the present invention are semiconducting surfaces, such as those based on p- or n-doped silicon, indium tin oxide (ITO), titanium oxide (TiO_x), boron-doped diamond and the like.

[0026] The properties of the surfaces to be modified with polymeric starting materials in accordance with the present invention can be tuned to a desired application. The modification can be carried out to tune such surface properties as roughness, hydrophilicity, hydrophobicity, surface charge, surface energy, biocompatibility and reactivity. For example, by choosing R_1 and R_2 as polar and/or ionic functional groups, such as an OH group and/or

a COOH group, the surface can be made hydrophilic. By choosing R_1 and R_2 as hydrophobic groups such as alkyl, alkenyl and alkynyl groups, the surface can be made more hydrophobic. By choosing R_1 and R_2 as perfluoro compounds, the surface can be made highly oleophobic or lipophobic and hydrophobic. By choosing R_1 and R_2 as NH_2 and/or COOH and/or PO_4^{2-} , the surface can be made more hydrophobic. By choosing R_1 and/or R_2 as any amino acid such as lysine and valine, the surface can be rendered biocompatible. **[0027]** Methods of modifying surfaces with polymeric starting materials in accordance with the present invention involve electrochemical methods. Such methods generally lead to an electrochemically deposited thin film or coating on the surface being modified. Electrochemical methods of surface modification offer certain advantages over other known physical methods. Such advantages are a more confined nature of the coating, a more durable conformal coating, less time required for the coating process and better monitoring of the coating process.

[0028] Methods of modifying surfaces with polymeric starting materials in accordance with the present invention may be, for example, 1) preparing a solution comprising a polymeric starting material in accordance with the present invention; 2) immersing into the solution a surface to be modified; 3) applying an electrochemical signal to the solution; and 4) forming at least one thin film or coating on the surface being modified. The electrochemical signal can be, for example, a voltage, a voltage scan or a current.

[0029] The thin films or coatings formed by methods in accordance with the present invention can have any desired and practical thickness. The thickness can be in the range of as little as about one nanometer to as large as about hundreds of microns. The thin films or coatings described herein are also strongly adhered to the surface being modified. The methods in accordance with the present invention can be carried out in either aqueous media or in non-aqueous media, depending on the solubility of the polymer starting material.

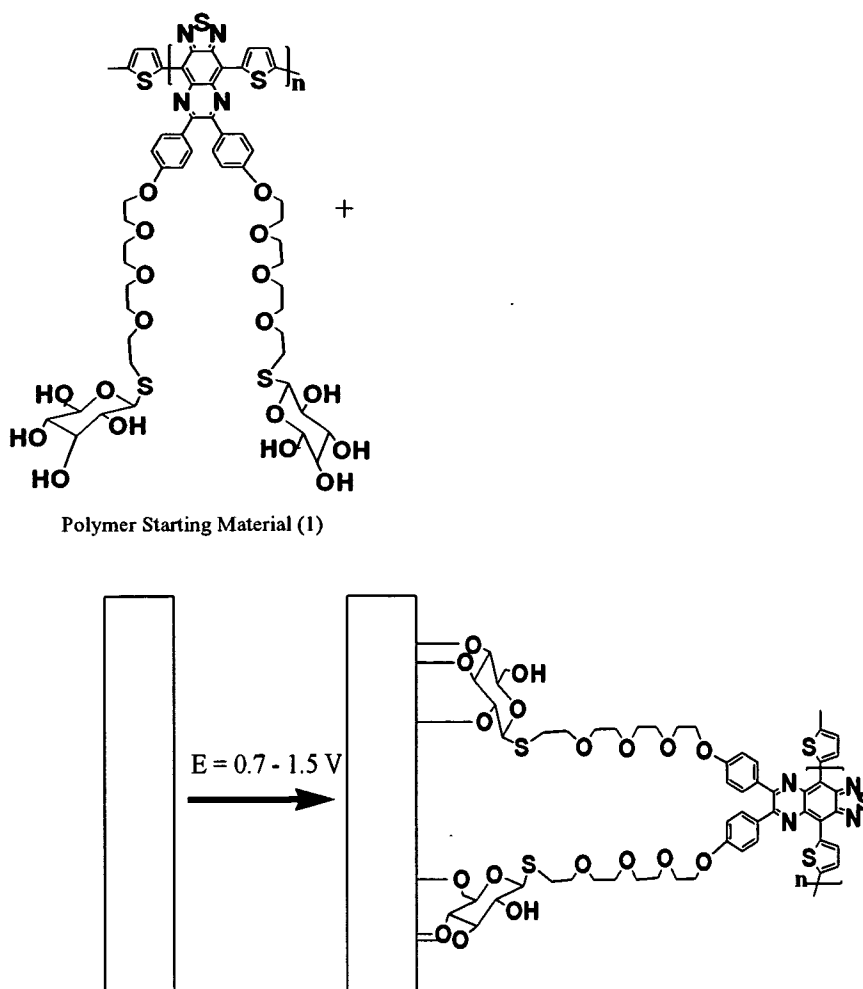
[0030] If desired, surfaces modified with the polymer starting materials according to the present invention can be further modified to further tune the properties of the system to a particular application. For example, surface bound polymers in accordance with the present invention can be further functionalized with highly conjugated molecules or metal complexes to form surface-coupled redox active molecules. Such surface-coupled redox active molecules can be, without limitation, ferrocene and derivatives thereof; bipyridine coordination complexes based on ruthenium, osmium, iron, or copper and derivatives thereof; and phenanthroline coordination complexes based on ruthenium, osmium, iron, or copper and derivatives thereof.

[0031] The concepts of the present invention will now be further described by reference to the following non-limiting examples of specific polymer starting materials and exemplary techniques for surface modification using the polymer starting materials. It should be understood that additional polymers and additional techniques of formation are also comprehended by the present invention.

Example 1: Surface Modification with Polymer Starting Material

(1)

[0032] Scheme 1 below illustrates the modification of an electrode surface with Polymer Starting Material 1. Without wishing to be bound by any particular theory, it is contemplated that Polymer Starting Material 1 binds to a given surface through the oxygen atoms of the -OH groups of the glucose moiety. Other binding mechanisms (such as binding through the N and/or S molecules of the heterocyclic moiety or C of the conjugated polymer backbone) may also be contemplated.

Scheme 1

[0033] Polymer Starting Material 1 was added to a 0.1 M NaClO₄ aqueous solution. The solution is then transferred to an electrochemical vessel adapted for cyclic voltammetry with a standard three-electrode setup using glassy carbon as the working electrode, platinum as the counter electrode and Ag/AgCl (saturated KCl) as the reference electrode. The electrodes are then immersed in the solution and a voltage, generally between 0.2 - 2.5 V, or 0.7 - 1.5 V, is applied thereto, which induces formation of a thin film based on Polymer Starting Material 1 on at least one of the electrodes. The length of time that the voltage is applied can vary, for example, from 2-30 seconds,

5-60 seconds, or 1-10 minutes, depending on factors such as the electrode material and the reaction composition.

[0034] Polymer Starting Material (1) is identified to undergo electrochemical oxidation and subsequent thin film formation on carbon and metallic electrodes. Figure 1 shows cyclic voltammetry results for Polymer Starting Material (1) in a 0.1 M NaClO₄ aqueous solution. The solution was cycled twice. The solid line is representative of the first cycle and the dotted line is representative of the second cycle. The first cycling of the solution produces a broad peak at about 0.9 V. This peak suggests oxidation of the polymer. The second cycling of the solution reveals an absence, or marked decrease in magnitude, of the same peak at about 0.9 V and suggests film formation on carbon and metallic electrodes.

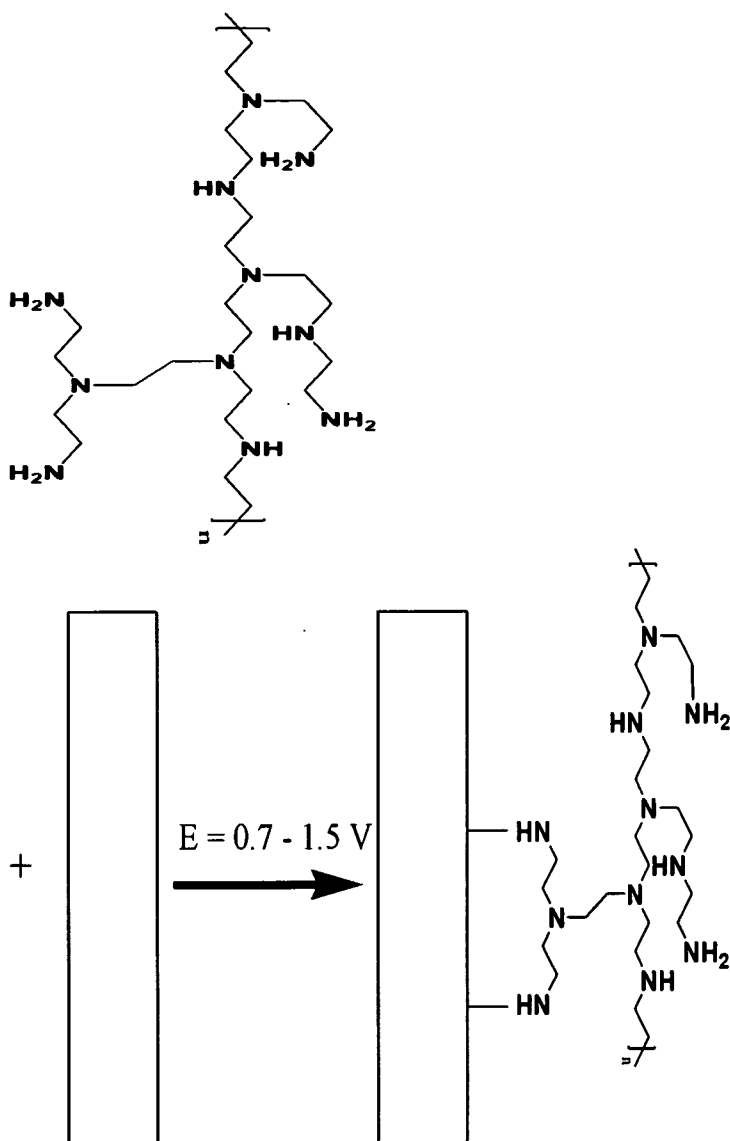
[0035] Figure 2 shows cyclic voltammetry results for Polymer Starting Material (1) in a 10 mM K₄[Fe(CN)₆]•3H₂O (potassium ferrocyanide) aqueous solution before and after thin film formation at a glassy carbon electrode. The solution was then cycled twice. The solid line is representative of the first cycle, e.g., before thin film formation at a glassy carbon electrode, and the dotted line is representative of the second cycle, e.g., after thin film formation at a glassy carbon electrode. The first cycling of the solution produces a peak current of about 325 μA. This peak suggests potassium ferrocyanide oxidation. The second cycling of the solution reveals a decrease in peak current to about 275 μA. The decrease in peak current of about 50 μA suggests a lower level of potassium ferrocyanide oxidation, which is consistent with thin film formation of Polymer Starting Material (1) on the glassy carbon electrode.

[0036] Figure 3 shows SEM images of a glassy carbon electrode before (Fig. 3A) and after (Fig. 3B) formation of a film thereon based on Polymer Starting Material (1). Figure 4 shows Energy-Dispersive X-Ray Spectroscopy (EDS) elemental analysis of the Polymer Starting Material (1) film on a glassy carbon electrode. The peaks at about 0.25, 0.40, 0.55 and

2.30 keV indicate the presence of C, N, O and S, respectively, from Polymer Starting Material (1).

Example 2: Surface Modification with Polymer Starting Material (2)

- 5 **[0037]** Scheme 2 below illustrates the modification of an electrode surface with Polymer Starting Material 2. Without wishing to be bound by any particular theory, it is contemplated that Polymer Starting Material 2 binds to a given surface through the nitrogen atoms of the amine side chains. Other binding mechanisms (such as binding through the nitrogen atoms in the
- 10 polymer chain) may also be contemplated.

Scheme 2

Polymer Starting Material (2)

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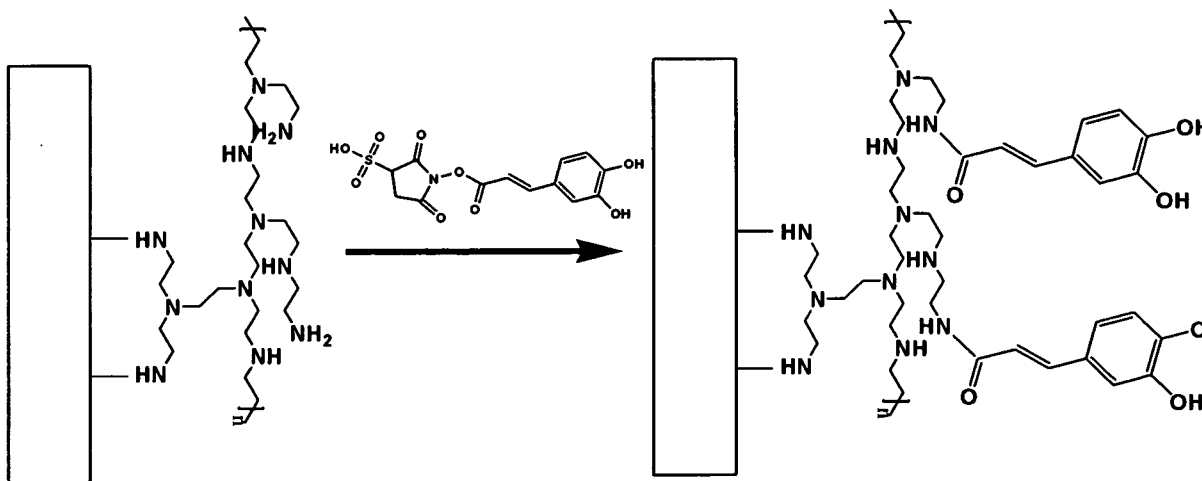
[0038] Polymer Starting Material 2 was added to a 0.1 M NaClO_4 aqueous solution. The solution is then transferred to an electrochemical vessel adapted for cyclic voltammetry with a standard three-electrode setup using glassy carbon as the working electrode, platinum as the counter electrode and Ag/AgCl (saturated KCl) as the reference electrode. The electrodes are then immersed in the solution and a voltage, generally between 0.7 - 1.5 V, is applied thereto, which induces formation of a thin film based on Polymer Starting Material 2 on at least one of the electrodes.

[0039] Polymer Starting Material (2) has been identified to undergo electrochemical oxidation and subsequent film formation on a carbon electrode. Figure 5 shows cyclic voltammetry results for Polymer Starting Material (2) in a 0.1 M NaClO₄ aqueous solution. The solution was cycled twice. The solid line is representative of the first cycle and the dotted line is representative of the second cycle. The first cycling of the solution produces a broad peak at about 0.85 V. This peak suggests oxidation of the polymer. The second cycling of the solution reveals an absence of the same peak at about 0.85 V and suggests film formation on a carbon electrode.

Example 3: Surface-Coupled Redox Active Molecules

[0040] Scheme 3 below illustrates further modification of the modified electrode surface of Example 2 with caffeic acid, such that the final thin film comprises at least one fragment of a caffeic acid molecule. A fragment being characterizable as a portion that can undergo a redox reaction through electron transfer with the electrode.

Scheme 3



[0041] Caffeic acid can be dissolved in any appropriate solvent to form a solution in which the Polymer Starting Material (2) modified surface is immersed. The reaction shown in Scheme 3 can be carried out in a buffer solution comprising 0.1 M 2-(N-morpholino)ethanesulfonic acid (MES) and 0.5 M NaCl at a pH of about 6.1. The reaction can be carried out at room

temperature for about 120 minutes. Figure 6 shows cyclic voltammetry results, in 0.1 M NaClO₄ aqueous solution, for a Polymer Starting Material (2)-caffeic acid modified surface. The solution was cycled once. The peak at about 0.5 V is indicative of oxidation of caffeic acid and the results are suggestive of the presence of surface-coupled redox active caffeic acid molecules.

[0042] Any numbers expressing quantities of ingredients, constituents, reaction conditions, and so forth used in the specification are to be understood as being modified in all instances by the term "about".

10 Notwithstanding that the numeric ranges and parameters setting forth, the broad scope of the subject matter presented herein are approximations, the numerical values set forth are indicated as precisely as possible. Any numerical value, however, may inherently contain certain errors or inaccuracies as evident from the standard deviation found in their respective

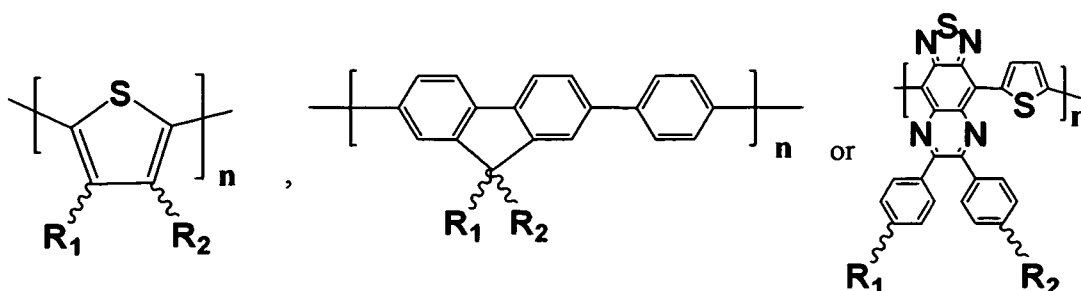
15 measurement techniques. None of the features recited herein should be interpreted as invoking 35 U.S.C. §112, ¶6, unless the term "means" is explicitly used.

[0043] Although the present invention has been described in connection with preferred embodiments thereof, it will be appreciated by those skilled in the

20 art that additions, deletions, modifications, and substitutions not specifically described may be made without departing from the spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. A thin film comprising at least one of:



wherein:

~~~~~ = oligo- or poly- ethylene glycol, an optionally substituted alkyl chain or an optionally substituted conjugated chain;

10 n = any integer greater than 1;

R<sub>1</sub> and/or R<sub>2</sub> = H, alkyl, alkene, alkyne, OH, Br, Cl, I, F, SH, COOH, NH<sub>2</sub>, CHO, maleimide, NHS ester, a heterocyclic compound that can form a metal complex, a carbohydrate, a protein, a peptide, DNA, RNA, an antibody, an antigen, an enzyme, a bacteria, a redox molecule, a host molecule, a guest molecule, a hapten, a lipid, a microbe, an aptamer, or a sugar;

15

wherein R<sub>1</sub> can be the same or different as R<sub>2</sub>; and

wherein at least one of R<sub>1</sub> and R<sub>2</sub> is NH<sub>2</sub>, COOH, OH or SH.

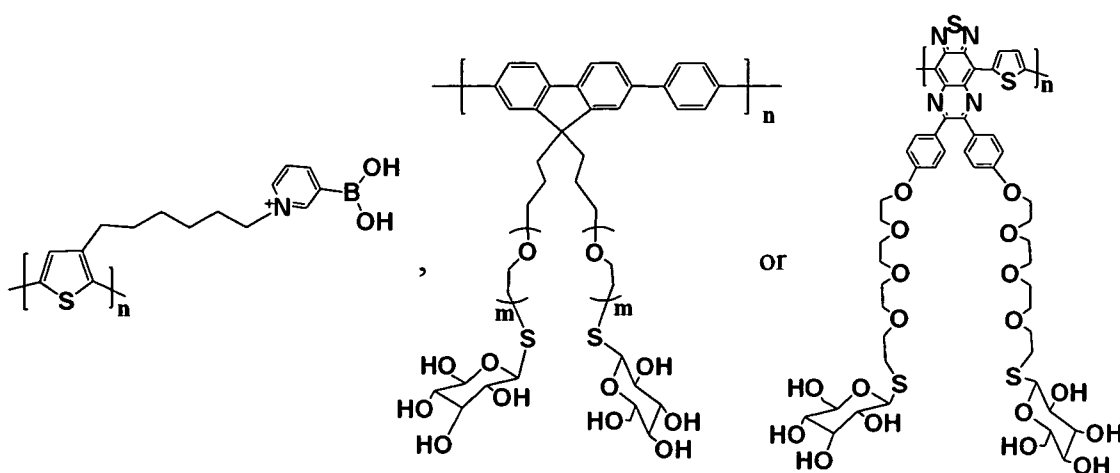
- 20 2. The thin film of Claim 1, wherein the thin film has a thickness from about 1 nm to about 1 μm.

3. A composition comprising a thin film of Claim 1, in combination with a surface comprising carbon, at least one metal, or at least one semiconductor.
- 25

4. The composition of Claim 3, wherein the surface is a carbon electrode or a metallic electrode.

5. The thin film of Claim 1, wherein the thin film is deposited by an electrochemical method.

6. A thin film comprising at least one of:



wherein  $n$  is any integer greater than 1 and  $m$  is 0 or an integer greater than 1.

7. The thin film of Claim 6, wherein the thin film has a thickness from about 1 nm to about 1  $\mu\text{m}$ .

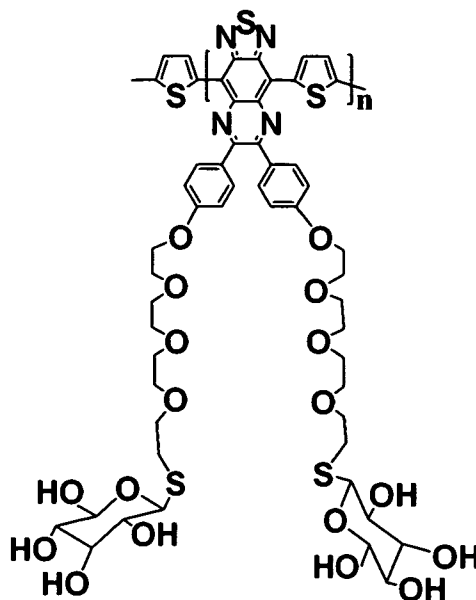
8. A composition comprising a thin film of Claim 6, in combination with a surface comprising carbon, a surface comprising at least one metal, or a surface comprising at least one semiconductor.

9. The composition of Claim 8, wherein the surface is a carbon electrode, a metallic electrode, or a semiconductor electrode.

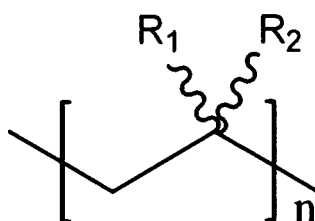
10. The thin film of Claim 6, wherein the thin film is deposited by an electrochemical method.

11. The thin film of Claim 6, wherein the thin film comprises:

5



12. A thin film comprising:



10

wherein:

~~~~~ comprises one of: an oligo- or poly- ethylene glycol, an optionally substituted alkyl chain and an optionally substituted conjugated chain;

15 n is any integer greater than 1; and

R₁ and/or R₂ = H, alkyl, alkene, alkyne, OH, Br, Cl, I, F, SH, COOH, NH₂, CHO, maleimide, NHS ester, a heterocyclic compound that can form a

metal complex, a carbohydrate, a protein, a peptide, DNA, RNA, an antibody, an antigen, an enzyme, a bacteria, a redox molecule, a host molecule, a guest molecule, a hapten, a lipid, a microbe, an aptamer, or a sugar;

5 wherein R_1 can be the same or different as R_2 ; and

wherein at least one of R₁ and R₂ is NH₂, COOH, OH or SH.

13. The thin film of Claim 12, wherein the thin film has a thickness from about 1 nm to about 1 μm .

10 14. A composition comprising a thin film of Claim 12, in combination with
a surface comprising carbon or a surface comprising at least one metal.

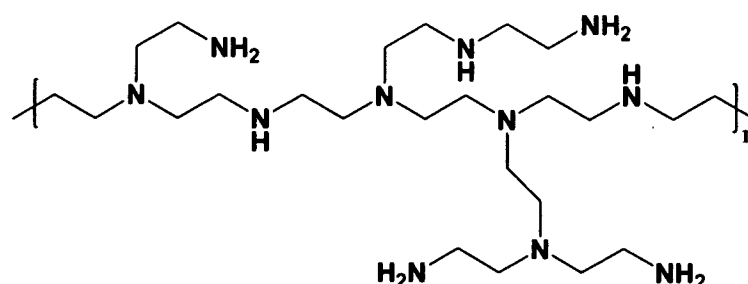
15. The composition of Claim 14, wherein the surface is a carbon electrode or a metallic electrode.

15

16. composition of Claim 14, wherein the thin film is deposited by an electrochemical method.

17. The thin film of Claim 12, wherein the thin film further comprises at
20 least one fragment of a caffeic acid molecule.

19. A thin film comprising:



25

wherein n is any integer greater than 1.

20. The thin film of Claim 19, wherein the thin film has a thickness from about 1 nm to about 1 μm .

21. A composition comprising a thin film of Claim 19, in combination with a surface comprising carbon, a surface comprising at least one metal, or a surface comprising at least one semiconductor.

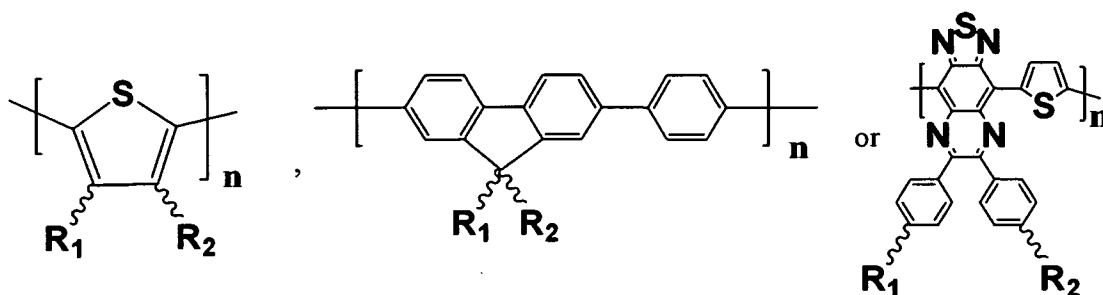
22. The composition of Claim 21, wherein the surface is a carbon electrode or a metallic electrode.

23. The thin film of Claim 21, wherein the thin film is deposited by an electrochemical method.

24. The thin film of Claim 19, wherein the thin film further comprises at least one fragment of a caffeic acid molecule.

25. A method of making a thin film comprising:

1) preparing a solution comprising one of:



wherein:

$\sim$ = oligo- or poly- ethylene glycol, an optionally substituted alkyl chain or an optionally substituted conjugated chain;

n = any integer greater than 1;

R_1 and/or R_2 = H, alkyl, alkene, alkyne, OH, Br, Cl, I, F, SH, COOH, NH_2 , CHO, maleimide, NHS ester, a heterocyclic compound that can form a

metal complex, a carbohydrate, a protein, a peptide, DNA, RNA, an antibody, an antigen, an enzyme, a bacteria, a redox molecule, a host molecule, a guest molecules, a hapten, a lipid, a microbe, an aptamer, or a sugar;

5 wherein R_1 can be the same or different as R_2 ;
 wherein at least one of R_1 and R_2 is NH_2 , $COOH$, OH or SH ;

 2) immersing into the solution at least one surface;
 3) applying an electrochemical signal to the solution; and
10 4) forming at least one thin film or coating on the surface.

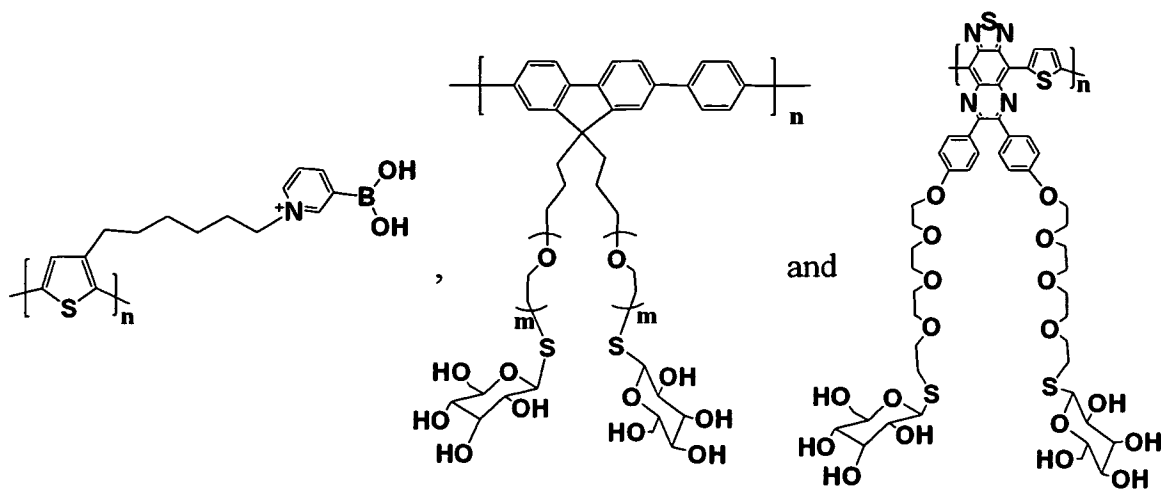
26. The method of Claim 25, wherein the thin film has a thickness from about 1 nm to about 1 μm .

15 27. The method of Claim 25, wherein the surface comprises carbon, at least one metal, or at least one semiconductor.

28. The method of Claim 27, wherein the surface is a carbon electrode, a metallic electrode, or a semiconductor electrode.

20 29. The method of Claim 27, wherein applying an electrochemical signal comprises applying a voltage, a voltage scan or a current.

30. A method of making a thin film comprising:
25 1) preparing a solution comprising one of:



wherein n is any integer greater than 1 and m is 0, 1 or an integer greater than 1, and

- 5 2) immersing into the solution at least one surface;
- 3) applying an electrochemical signal to the solution; and
- 4) forming at least one thin film or coating on the surface.

31. The method of Claim 30, wherein the thin film has a thickness from
10 about 1 nm to about 1 μm .

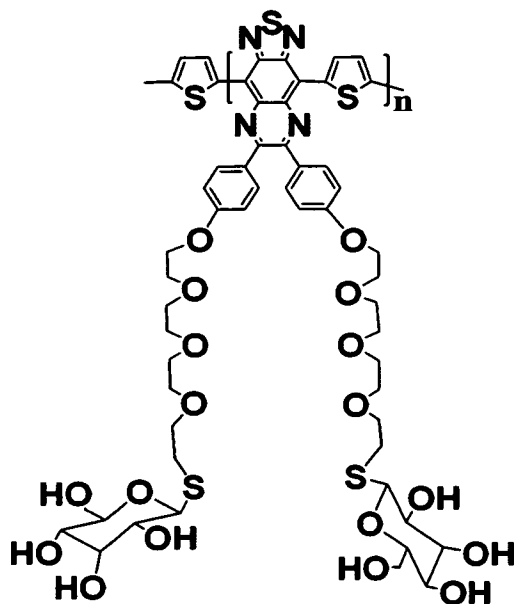
32. The method of Claim 30, wherein the surface comprises carbon, at least one metal, or at least one semiconductor.

15 33. The method of Claim 30, wherein the surface is a carbon electrode, a metallic electrode, or a semiconductor electrode.

34. The method of Claim 30, wherein applying an electrochemical signal comprises applying a voltage, a voltage scan or a current.

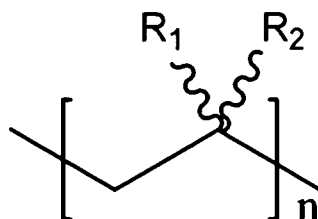
20

35. The method of Claim 30, wherein the thin film comprises:



36. A method of making a thin film comprising:
1) preparing a solution comprising:

5



wherein:

~~~~~ comprises one of: an oligo- or poly- ethylene glycol, an optionally substituted alkyl chain and a conjugated chain;

10 n is any integer greater than 1; and

R<sub>1</sub> and/or R<sub>2</sub> = H, alkyl, alkene, alkyne, OH, Br, Cl, I, F, SH, COOH, NH<sub>2</sub>, CHO, maleimide, NHS ester, a heterocyclic compounds that can form a metal complex, a carbohydrate, a protein, a peptide, DNA, RNA, an antibody, an antigen, an enzyme, a bacteria, a redox molecule, a host  
15 molecule, a guest molecule, a hapten, a lipid, a microbe, an aptamer or a sugar;

wherein R<sub>1</sub> can be the same or different as R<sub>2</sub>; and

wherein at least one of R<sub>1</sub> and R<sub>2</sub> is NH<sub>2</sub>, COOH, OH or SH;

- 2) immersing into the solution at least one surface;
- 3) applying an electrochemical signal to the solution; and
- 4) forming at least one thin film or coating on the surface.

5

37. The method of Claim 36, wherein the thin film has a thickness from about 1 nm to about 1  $\mu\text{m}$ .

38. The method of Claim 36, wherein the surface comprises carbon, at  
10 least one metal, or at least one semiconductor.

39. The method of Claim 36, wherein the surface is a carbon electrode, a metallic electrode, or a semiconductor electrode.

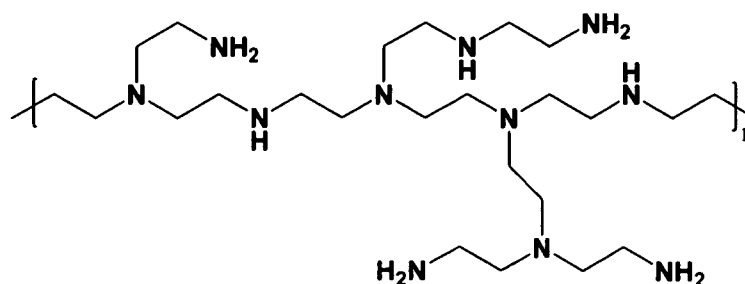
15 40. The method of Claim 36, wherein applying an electrochemical signal comprises applying a voltage, a voltage scan or a current.

41. The method of Claim 36, wherein the thin film further comprises at least one fragment of a caffeic acid molecule.

20

42. A method of making a thin film comprising:

1) preparing a solution comprising:



25     wherein  $n > 1$ ;

2) immersing into the solution at least one surface;

- 3) applying an electrochemical signal to the solution; and
- 4) forming at least one thin film or coating on the surface.

43. The method of Claim 42, wherein the thin film has a thickness from  
5 about 1 nm to about 1  $\mu\text{m}$ .

44. The method of Claim 42, wherein the surface comprises carbon, at least one metal, or at least one semiconductor.

10 45. The method of Claim 42, wherein the surface is a carbon electrode, a metallic electrode, or a semiconductor electrode.

46. The method of Claim 42, wherein applying an electrochemical signal comprises applying a voltage, a voltage scan or a current.

15

47. The method of Claim 42, wherein the thin film further comprises at least one fragment of a caffeic acid molecule.

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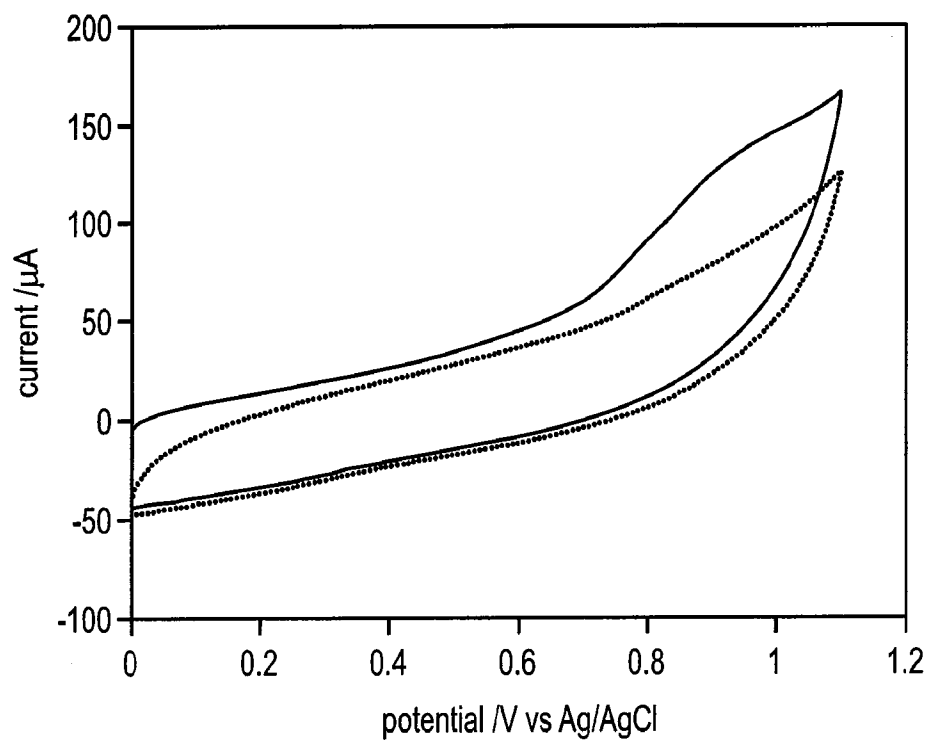


FIG. 1

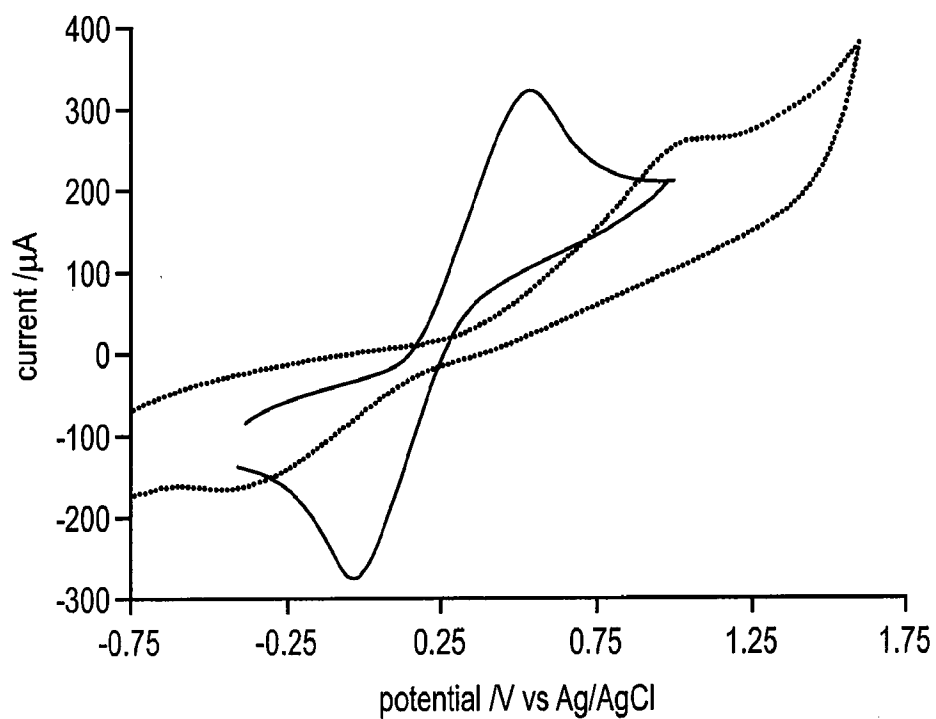


FIG. 2

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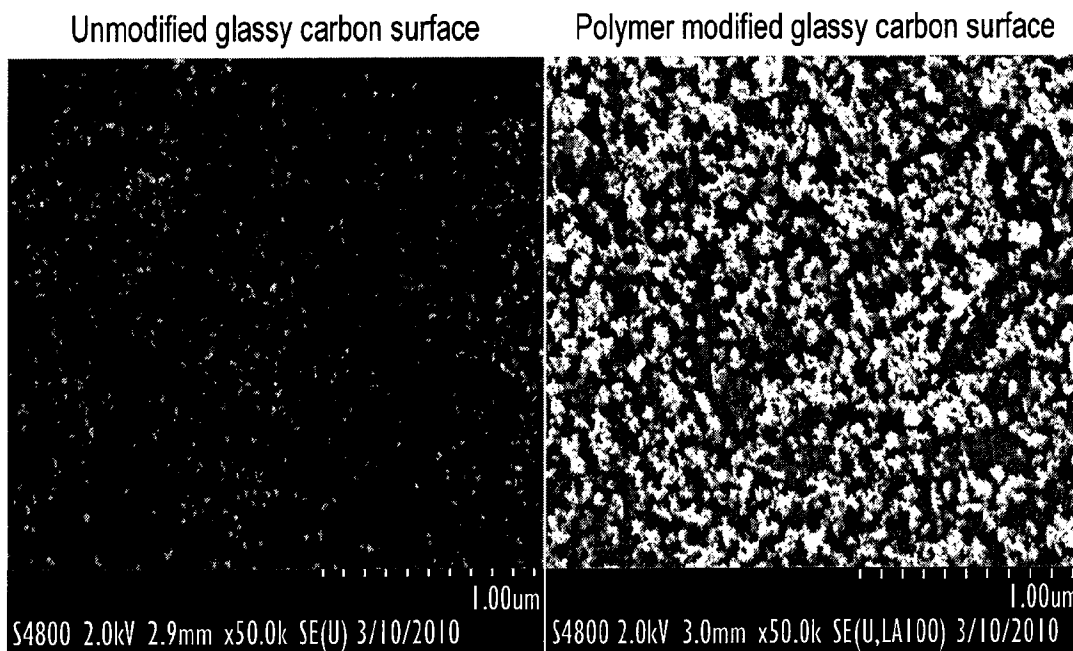


FIG. 3A

FIG. 3B

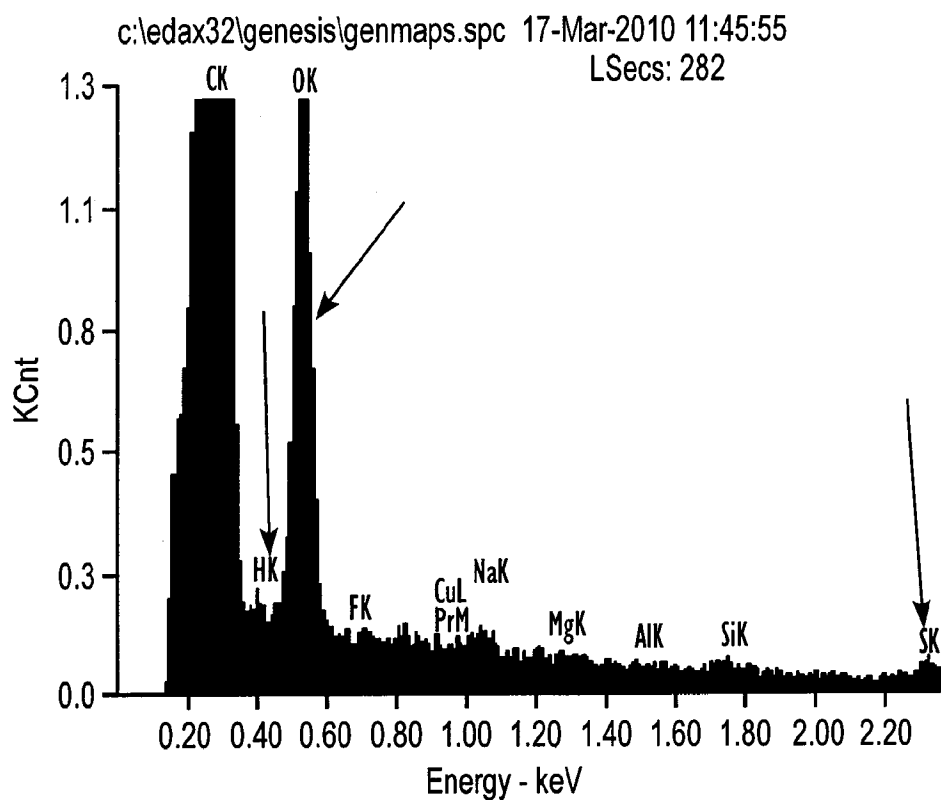


FIG. 4

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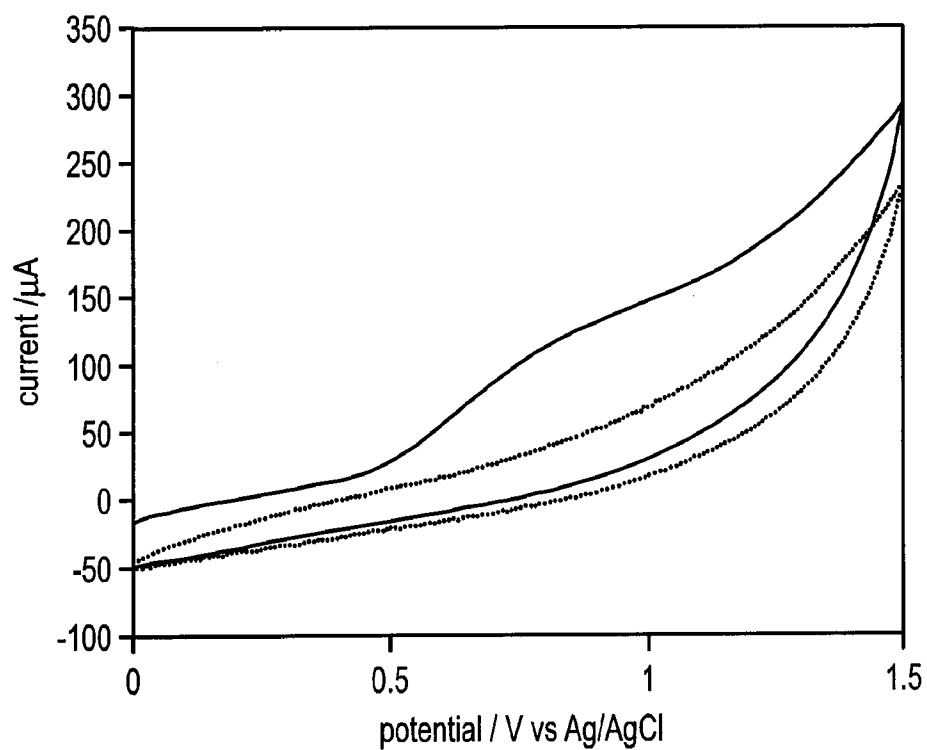


FIG. 5

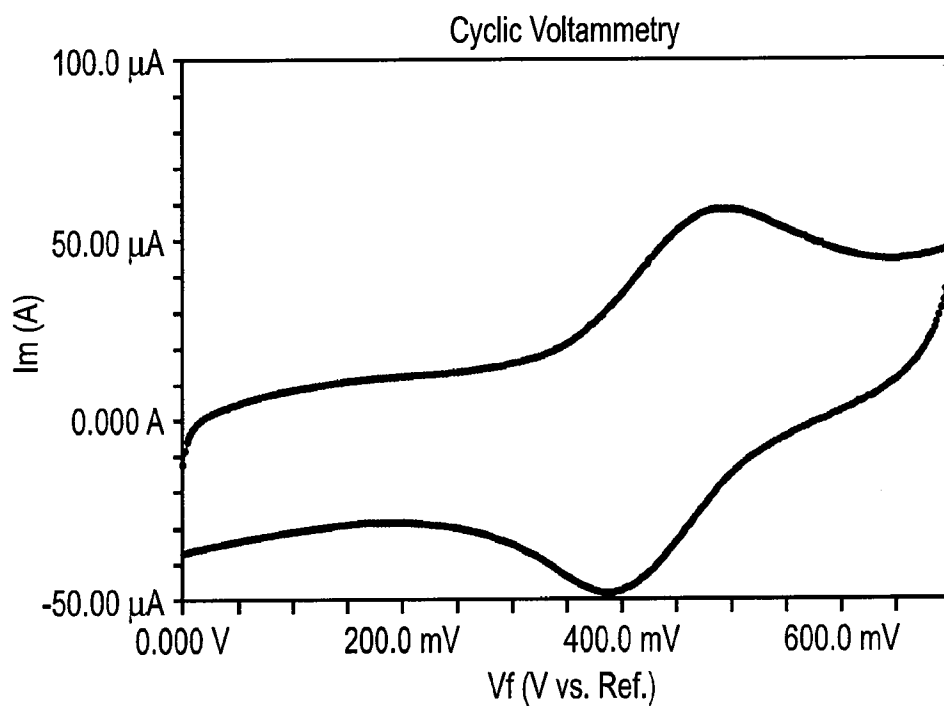


FIG. 6

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/00173

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01B 1/12 (2012.01)

USPC - 252/500

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)

IPC(8) -H01B 1/12 (2012.01)

USPC -252/500

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
PubWest, Google Patent, Google Scholar, WIPO (thick, thickness, fluorene, thiophene, deposit, immerse, conjugated, polymer, voltage, semiconductor, glycol, thin, film, electrode, alkyl, surface, benzothiadiazole, benzathiadiazole, formula, structure, electrochemical, solution, xylose)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category*       | Citation of document, with indication, where appropriate, of the relevant passages                                                                                    | Relevant to claim No.      |
|-----------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------|
| X<br>-----<br>Y | US 2010/0327271 A1 (UETANI) 30 December 2010 (30.12.2010) entire document, especially para[0015]-[0016], [0027], [0133], [0135], [0137]-[0138], [0140], [0142]-[0143] | 1-2<br>-----<br>3-5, 25-29 |
| Y               | US 2008/0248313 A1 (SESHADRI, et al.) 09 October 2008 (09.10.2008) entire document, especially para[0211]-[0212], [0230]-[0231], [0285], [0295]                       | 3-4, 7-9                   |
| Y               | US 2009/0293946 A1 (LIN, et al.) 03 December 2009 (03.12.2009) entire document, especially para[0021], [0024]-[0025]                                                  | 5, 10, 25-35               |
| Y               | US 2009/0221762 A1 (THERIEN, et al.) 03 September 2009 (03.09.2009) entire document, especially para[0010], [0046]-[0047], [0065]-[0066]                              | 6-11, 30-35                |
| Y               | US 5,453,335 A (FAUTEUX, et al.) 26 September 1995 (26.09.1995) entire document, especially col 2, ln 26-19; col 6, ln 58-60; col 7, ln 9-25                          | 6-11, 30-25                |
| X               | US 2006/0237695 A1 (Williams et al.) 26 October 2006 (26.10.2006)<br>(Fig. 2; para [0129], [0184])                                                                    | 1-3                        |

☐ Further documents are listed in the continuation of Box C. ☐

\* 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 another 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

30 August 2012 (30.08.2012)

Date of mailing of the international search report

14 SEP 2012

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents  
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300  
PCT OSP: 571-272-7774

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/00173

## 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.:  
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:
  
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:

Group I: claims 1-11 and 25-35

Group II: claims 12-18 and 36-41

Group III: claims 19-24 and 42-47

see extra sheet for details

1. ☐ As all required additional 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 additional fees, this Authority did not invite payment of additional fees.
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.: 1-11 and 25-35

### 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

International application No.

PCT/US 12/00173

## Box No. III Observations where unity of invention is lacking (continuation)

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1.

Group I: claims 1-11 and 25-35, drawn to a thin film comprising a polymer [ with an unsaturated backbone structure ] made with at least one of the monomer units listed.

Group II: claims 12-18 and 36-41, drawn to a thin film comprising substituted polyethylene, as shown

Group III: claims 19-24 and 42-47, drawn to a thin film comprising a branched polyalkylamine skeleton with alkyl amine functionalization through tertiary amine, as shown.

The inventions listed as Groups I-III do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Groups II and III do not require an unsaturated backbone structure, as required by Group I.

Groups I and III do not require polyethylene backbone structure, as required by Group II.

Group I and II do not require polyalkylamine, as required by Group III.

Thus, the inventions listed as Groups I-III do not relate to a single general inventive concept under PCT Rule 13.1 because under PCT Rule 13.2 they lack the same or corresponding special technical feature.