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(54) Title: SENSOR

(57) Abstract: The invention provides a sensor component for detecting an analyte, comprising a first electrode and a second electrode; an insulating substrate disposed between the first electrode and the second electrode; a plurality of conductive nodes disposed on a surface of the insulating substrate; and a plurality of connector molecules comprising two or more groups capable of forming a chemical bond with a conductive node or an electrode, which connector molecules are capable of displaying a change in an electrical property in response to interaction with an analyte. At least some of the connector molecules are bonded to one or more nodes, or to one electrode, and thereby form electrical junctions between separate nodes or between a node and an electrode. The electrical junctions form an electrical percolation network comprising at least one continuous pathway of connector molecules between conductive nodes which connects the first electrode and the second electrode. Preferably, the network is in the percolation region. The invention also relates to a process for producing a sensor component, and a sensor component obtainable by that process. The invention also provides devices comprising the sensor component of the invention, including a sensor, as well as uses of the sensor component of the invention and uses of the devices of the invention, for detecting analytes.



SENSOR

FIELD OF THE INVENTION

The present invention relates to a sensor component for detecting an analyte and a process for producing a sensor component. The invention also relates to devices comprising the sensor component, including a sensor.

BACKGROUND OF THE INVENTION

Sensors for molecular analytes have a wide range of applications in many industries and services. In many fields the presence of sensors for certain analytes are of huge importance for the safety of people and equipment. Sensors for molecular analytes can be incorporated in alarms to warn of the occurrence of spillages or leaks of toxic compounds. For example, warehouses containing chemical storage or sites where there have been chemical spills require continuous measurement of the concentration of volatile compounds in the air. Sensors for molecular analytes can also be used to detect levels of compounds such as explosive compounds and chemical warfare agents. This has major applications on the battlefield, at security posts and in airports and tunnels. One important application is the detection of landmines by low level detection of the volatile compounds they contain.

Applications are also found for sensors for molecular analytes in medicinal fields. The detection of certain compounds in a patient's exhaled breath is one example.

It has been a long-standing goal to produce sensors with sensing components that are sensitive, selective, light, durable and cheap. Sensitivity at below the parts per million (ppm) threshold is desirable. Selectivity is one if the most significant factors controlling a sensor component's utility. If a sensor can be tailored to be selective for a single compound or group of compounds, detection of low levels of these analytes can be possible even in the presence of a wide range of other volatile compounds. Light weight and durable sensor components allow for mobile sensor systems useful in harsh conditions. If the sensor components can be produced at low cost this has the potential for cheap and disposable sensor systems which could be used, for example, for detecting landmines in post-conflict zones.

A wide range of sensors for molecular analytes are known. Some of the simplest sensors are paper based sensors coated in a compound which displays an observable change,

often a colour change, in the presence of an analyte. Although these sensors are generally easy to produce and low cost, they are typically single use and can display low sensitivity.

Analyte detection using spectroscopy can be an accurate approach which allows concentrations and compositions of volatile compounds to be established in many cases with near certainty. Such approaches are, however, in the most part hindered by insurmountable problems of cost and delicate yet immobile equipment. Spectroscopic techniques also often require highly skilled technicians for their operation.

Electrochemical sensor components have come to the fore in recent years. These sensor elements will generally contain a material which displays a change in an electrical property in the presence of an analyte. Examples of these include metal oxide based sensor components which can detect gaseous analytes by variations in conductivity. However, selectivity is often low and most metal oxide based sensor components need to operate at high temperatures.

Sensor components containing conjugated polymer molecules is an area of research which has grown rapidly in the past two decades. Conjugated organic polymer molecules can demonstrate a range of conductivities covering several orders of magnitude which can be highly sensitive to the presence of analytes. Conjugated polymers (CPs) can also be adapted for specific selectivity to certain analytes using pendant groups such as crown ethers. A range of functionalised CPs and their use in detectors are described in McQuage *et al.*, “Conjugated Polymer-Based Chemical Sensors,” *Chem. Rev.*, **100**, 2537-2574 (2000), Bai *et al.*, “Gas Sensors Based on Conducting Polymers,” *Sensors*, **7**, 267-307 (2007) and Rahman *et al.*, “Electrochemical Sensors Based on Organic Conjugated Polymers,” *Sensors*, **8**, 118-141 (2008).

These CP based sensor elements are generally based on thin films of the CP deposited on an insulating substrate. Measurement configurations for such CP thin film components are described in Lange *et al.*, “Chemiresistors based on conducting polymers: A review on measurement techniques,” *Analytica Chimica Acta*, **687**, 105-113 (2011).

As discussed above, CPs can be modified for selectivity for specific analytes. Examples of modified CPs are given in Lange *et al.*, “Conducting polymers in chemical sensors and arrays,” *Analytica Chimica Acta*, **614**, 1-26 (2008). CPs can be modified with groups as far ranging as antibodies.

Thin film CP sensor elements still have several drawbacks. In particular, increased sensitivity is desirable. Thin film sensors often have to employ more complicated electrode configurations including components such as back-gates in order to amplify what are often small signals produced by analytes.

5 In US 7,824,619 a sensor is described in which single molecules are used to create nano-junctions between a pair of electrodes. Although this method may afford some increased sensitivity, none of the potential of using a percolation network has been explored.

Thin film CP sensors comprising carbon nanotubes (CNTs) dispersed in the polymer are considered in Wang *et al.*, "Carbon Nanotube/Polythiophene Chemiresistive Sensors for
10 Chemical Warfare Agents," *JACS*, 130, 5392-5393 (2008). Although the CNTs are said to form a 'percolative network', the network is based on a dispersion of CNTs within a polymer thin film comprising a continuous mass of polymer between the two electrodes. Such a network would not be able to take advantage of the potential for critical behaviour in percolation networks. Similar systems are discussed in Wang *et al.*, "Molecular Recognition
15 for High Selectivity in Carbon Nanotube/Polythiophene Chemiresistors," *Angew. Chem. Int. Ed.*, 47, 8394-8396 (2008).

US 2010/0180691 relates to a method of measuring strain in a geosynthetic product by using a mixture of a polymeric material and an electrically conductive filler as a percolation network.

20 Semi-regular arrays of current-conducting elements formed of electrically conducting molecules between electrically conducting islands are disclosed in US 6,812,117. These networks are used in the formation of electrical circuitry and do not operate at an electrochemical level.

SUMMARY OF THE INVENTION

25 The present inventor has found that by departing from the standard thin film model of electrochemical sensors and producing a network of analyte-sensitive connector molecules forming what is known as an "electrical percolation network" in or near the "percolation region", sensors of extremely high sensitivity can be formed. Conjugated polymers are an example of connector molecules which could be used in the sensor component of the
30 invention.

The invention provides a sensor component for detecting an analyte comprising:

- (i) a first electrode and a second electrode;
- (ii) an insulating substrate disposed between the first electrode and the second electrode;
- 5 (iii) a plurality of conductive nodes disposed on a surface of the insulating substrate; and
- (iv) a plurality of connector molecules comprising one or more groups capable of forming a chemical bond with a conductive node or an electrode, wherein the connector molecules are capable of displaying a change in an electrical property in response to
- 10 interaction with an analyte;

wherein at least some of the connector molecules are bonded to one or more nodes, or to one electrode, and thereby electrical junctions are formed between separate nodes or between a node and an electrode;

- 15 wherein the electrical junctions form an electrical percolation network, which electrical percolation network comprises at least one continuous pathway of connector molecules and conductive nodes which connects the first electrode and the second electrode.

Generally, the number (e.g. areal density) of connector molecules in the electrical percolation network is such that the percolation network is in the percolation region with respect to the change of an electrical property of the connector molecules upon interaction

20 with an analyte.

The invention also provides a process for producing a sensor component for detecting an analyte, the process comprising:

- (a) providing an insulating substrate having a plurality of conductive nodes disposed on a surface thereof, which insulating substrate is disposed between a first electrode
- 25 and a second electrode;

- (b) disposing connector molecules onto the substrate and thereby forming electrical junctions between separate conductive nodes or between an electrode and a conductive node, and monitoring an electrical property between the first electrode and the second electrode,

- 30 which connector molecules comprise two or more groups capable of forming a chemical bond with a conductive node or an electrode, and wherein the connector molecules are capable of displaying a change in an electrical property in response to interaction with an analyte; and

(c) ceasing to dispose the connector molecules when the change in the electrical property indicates that an electrical percolation network has formed.

Usually, step (c) comprises ceasing to dispose the connector molecules when the change in the electrical property indicates that the electrical percolation network is formed in the percolation region.

The invention also provides a sensor component which is obtainable by the process of the invention for producing a sensor component.

The invention also provides a device comprising a sensor component of the invention.

The device may be a sensor, an alarm, a warning system, a detector, a spectrometer, a kit, a transistor or a diode. Typically the device is a sensor. The device usually further comprises a detection means operably connected to the first and second electrodes of the sensor component. The detection means is typically capable of detecting a change in an electrical property of the sensor component due to the interaction of an analyte with the connector molecules. Usually, the detection means is capable of detecting a change in an electrical property of the sensor component by measuring, for example, resistance, conductance, impedance, capacitance, or magneto-resistance.

The invention also provides the use of a device according to the invention for detecting an analyte.

The invention also provides a process for producing a plurality of conductive nodes on a surface of an insulating substrate, which process comprises:

- (a) providing an insulating substrate disposed between a first electrode and a second electrode;
- (b) disposing a layer of a conductive node material on a surface of the insulating substrate wherein the conductive node material wets the surface and connects the electrodes;
- and
- (c) dewetting the layer of conductive node material to form isolated nodes of the conductive node material on the insulating substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic cartoon demonstrating an electrical percolation network on a square lattice of nodes (a) below, (b) near, and (c) above the percolation threshold. The solid

rectangles marked by + and – represent electrodes. The light lines represent connections between nodes in the square lattice. The bold lines highlight connection pathways between the two electrodes at each of the stages.

Figure 2 is a hypothetical graph showing variations in an electrical property (vertical axis) for an idealised electrical percolation network as the areal density of connector molecules between adjacent nodes (horizontal axis) increases. The percolation region (A) and thin film limit (B) are also indicated.

Figure 3 is a scanning electron microscopy (SEM) image showing the morphology of 4.5 to 5 nm thick layer of Au deposited onto an MgO (001) single crystal using thermal evaporation.

Figure 4 is an SEM image showing the morphology of a network of Au nodes on the surface of an MgO (001) single crystal formed by annealing the 4.5 to 5 nm thick layer of Au shown in Figure 3 at 700°C under ultra-high vacuum (UHV).

Figure 5 is a graph showing the response of a Au network alone (control) and an Au-sexithiophene network to air. The vertical axis shows resistance (ohm). The horizontal axis shows time (s). A and B indicate two instances of “gas in and out” for the Au only network. C indicates the point at which α -sexithiophene deposition began. C indicates the point at which deposition stopped. E indicates an instance of “gas in and out” for the Au-sexithiophene network. The central portion of the graph (between 500 and 600 seconds) shows the controlled decrease in resistance of the network as α -sexithiophene is deposited on the surface.

Figure 6 is a graph showing the response of the Au-sexithiophene network to moisture (A1 indicates gas comprising moisture in and A2 indicates gas comprising moisture out) and alcohol (B1 indicates gas comprising alcohol in, B2 indicates gas comprising alcohol out). The vertical axis shows resistance (ohm). The horizontal axis shows time (s).

Figure 7 shows a resistance against time graph for a process of dewetting a 4.7 nm layer of Au on an MgO (001) single crystal between two Pt electrodes separated by 1mm. The smoothing (A), dewetting (B) and ripening (C) stages are indicated. The vertical axis shows resistance (ohm). The horizontal axis shows time (s).

Figure 8 shows an SEM image of 5 nm Au deposited on an MgO (001) single crystal substrate before annealing.

Figure 9 shows an SEM image of 5 nm Au deposited on an MgO (001) single crystal substrate after annealing at 700°C.

Figure 10 shows the change of resistance with increased deposition amount of sexithiophene onto the Au nanoparticle scaffold. The horizontal axis shows thickness of the deposited layer of sexithiophene (nm). The vertical axis shows resistance (ohm). The smooth curve shows a fit to the data.

Figure 11 shows the first derivative of the smooth curve fit for the change in resistance in Figure 10. The horizontal axis shows thickness of the deposited layer of sexithiophene (nm).

Figure 12 shows the sensing response for a sensor operating in the percolation regime (3.3 nm thickness of sexithiophene, upper curve, A) versus one operating in the thin film regime (23 nm thickness, lower curve, B). The testing gas was saturated H₂O vapour in a N₂ carrier gas at a total pressure of 5.5×10^{-4} Torr. The vertical axis shows resistance (ohm). The horizontal axis shows time (s).

Figure 13 shows the response from a Au-sexithiophene percolation sensor when the pressure of saturated H₂O vapour in a N₂ carrier gas is increased. Curve B relates to sensing at a pressure of 4×10^{-4} Torr. The pressure was then increased to 5.5×10^{-4} Torr as shown in curve A. The vertical axis shows resistance (ohm). The horizontal axis shows time (s).

Figure 14 shows the response of the percolation sensor to three different gasses, all at a pressure of 5.5×10^{-4} Torr. The response to N₂ (A), saturation vapour pressure of ethanol in N₂ (B), and saturated H₂O vapour in a N₂ carrier gas (C) is shown.

DETAILED DESCRIPTION OF THE INVENTION

Percolation theory is the study of fluid flow in random lattices and has applications in several scientific fields. In the context of electrical percolation, the theory concerns electrical properties, such as resistance, of random conducting networks. A simple example of an electrical percolation network would be a large two dimensional (2D) square lattice of pylons between two electrodes where there is a certain probability that any two adjacent pylons are connected by an electrical junction of some form. A schematic cartoon of such a network is given in Figure 1. In Figure 1 (a) a large number of connections between adjacent “pylons” (or “nodes”, represented by the vertices of the square lattice) has been made, but there is no continuous connection between the two electrodes and the network is not connected to both

electrodes. In Figure 1 (b) a greater number of connections is made between adjacent “pylons” and a single continuous pathway between the two electrodes is formed. The instance at which the first continuous connecting pathway is formed is known as the “percolation threshold”. The percolation threshold is more formally defined for an infinite
5 percolation network as the probability that two adjacent nodes are connected which gives rise to a “giant connected component” in the network, but the analogy with a finite network is clear.

Figure 1 (c) demonstrates how, when only a few new connections are made between adjacent “pylons”, a large number of new continuous pathways between the two electrodes
10 may be formed once the network is past the percolation threshold. A small change in the number of connections between nodes can cause a large change in the number of continuous connecting pathways between the two electrodes. This is a distinctive feature of electrical percolation networks which the present invention takes advantage of: there is a region called the “percolation region” in which electrical properties such as conductance, impedance and
15 capacitance of the network will change rapidly as the number of connections increases (the behaviour of the electrical property is non-linear in this region). Within this region, some electrical properties of the network are critically dependent on the number of connections in the electrical percolation network. This region is highlighted on the hypothetical graph in Figure 2.

The “thin film limit” is also indicated on the graph in Figure 2. In the context of the present invention, as the areal density of connector molecules (e.g. conjugated polymer molecules) increases the network will essentially become a thin film of the connector molecules as the connector molecules exposed to the analyte form a thin film (possibly where the thin film is over the top of the percolation network). Thin film electrochemical sensors
20 are well known as described in the references above and, as can be seen from Figure 2, the change in electrical properties of sensors in this limit are much less sensitive on changes in the connectivity of the network.

An example of an electrical percolation network is given in “Percolation threshold model and its application to the electrical conductivity of layered $\text{BaTiO}_3\text{-Ni}$,” M. Ambrožič,
30 A. Dakskobler, M. Valant, T. Kosmač, *Material Sciences Poland*, 23, 2 (2005) wherein a summary of the features of electrical percolation networks is given: “when electrically conducting particles are randomly distributed within an insulating matrix such as metal-

ceramic matrix composites, the sample is non-conducting, until the volume fraction of the conducting phase reaches the so-called percolation threshold. In addition, close to the percolation threshold, the electrical properties show a non-linear (critical) behaviour: small variations in the physical parameters, such as composition, voltage or temperature, result in large variations of electrical properties.”

The above outlines the idea behind an electrical percolation network based sensor element. As to how it is put in to practice is now described. In the present invention the “pylons” are nodes of a conducting material disposed on an insulating surface. The junctions between nodes are formed by one or more connector molecules which display a change in an electrical property (such as resistance, conductance, capacitance, permeability, permittivity or magneto-resistance) in response to interaction with an analyte. The connector molecules are bonded at one of their ends to a node or an electrode. The connections between nodes are formed by one or more connector molecules. Some of the connector molecules may be bonded at both of their ends to two separate nodes. The sensor component can be produced in such a way that the number of connector molecules disposed on the lattice of conductive nodes is such that the electrical percolation network formed is in the percolation region. The analyte sensitivity of the sensor component arises because analyte molecules, ranging from simple diatomic gases to complex organic molecules, interact with the connector molecules, changing an electrical property and effectively “switching-on” or “switching-off” (depending on the analyte, the connector molecules and the electrical property measured) connections between the nodes. For instance, in some cases, the analyte might interact with the connector molecules and reduce their conductivity. In an electrical percolation network of these connector molecules, the presence of this analyte would lead to a rapid, non-linear increase in the resistivity of the sensor element. In contrast, a thin film of such connector molecules would only demonstrate a slow, linear increase in resistivity due to a presence of the analyte.

These principles can apply to any electrical property (such as resistance, conductance, capacitance, permeability, permittivity or magneto-resistance), and in all cases the property may either increase or decrease in the presence of an analyte depending on the constituents of the connector molecules and the analyte.

The invention is now described in detail.

The invention provides a sensor component for detecting an analyte comprising:

- (i) a first electrode and a second electrode;

(ii) an insulating substrate disposed between the first electrode and the second electrode;

(iii) a plurality of conductive nodes disposed on a surface of the insulating substrate; and

5 (iv) a plurality of connector molecules comprising two or more groups capable of forming a chemical bond with a conductive node or an electrode, wherein the connector molecules are capable of displaying a change in an electrical property in response to interaction with an analyte;

10 wherein at least some of the connector molecules are bonded to one or more nodes, or to one electrode, and electrical junctions are formed between separate nodes or between a node and an electrode; and

15 wherein the electrical junctions form an electrical percolation network over the insulating substrate, which electrical percolation network comprises at least one continuous pathway of connector molecules and conductive nodes which connects the first electrode and the second electrode.

Often, at least some of the connector molecules are bonded to two or more nodes, or to one electrode and one or more nodes, and form electrical junctions between separate nodes or between a node and an electrode.

20 The electrical percolation network is typically between the percolation threshold and the thin-film limit. In particular, the electrical percolation network is typically in the percolation region.

25 Thus, usually, the number and configuration of junctions in the electrical percolation network is such that the percolation network is between the percolation threshold and the thin-film limit. The number and configuration of the junctions is directly proportional to the number of connector molecules deposited and therefore the areal density of the connector molecules.

30 Typically, the number and configuration of junctions (or number of connector molecules) in the electrical percolation network is such that the percolation network is in the percolation region with respect to the change of an electrical property of the connector molecules upon interaction with an analyte. This is the region in which the electrical

property varies most rapidly as the number of connector molecules disposed on the surface changes (i.e. as the areal density changes).

Often, the number of connector molecules in the percolation network is such that an electrical property varies most rapidly as a function of the number of connector molecules present in the percolation network.

The term “percolation”, as used herein, refers to the movement of a substance or particle through pathways in a random network. The particles in the case of the present invention will generally be electrons carrying an electric current. The term “percolation network”, as used herein, refers to a random network of pathways and connections through which a substance or particle may percolate. The percolation network related to the present application is disposed between at least two electrodes.

The term “percolation threshold”, as used herein, refers to the point at which the number of connector molecules and junctions in the percolation network is such that a single, continuous pathway of connector molecules and conductive nodes is formed across the percolation network. In the context of the present invention (a finite percolation network), this continuous pathway will connect the first and second electrodes between which the network is disposed. The continuous pathway comprises connector molecules and conductive nodes.

The percolation threshold for an infinite lattice may be defined by a single value, p , which is the probability that a bond connecting two nodes of the lattice is occupied (this is known as bond percolation; there is another form of percolation known as site percolation but this is less relevant to the present invention). Thus, in percolation theory, the percolation threshold is formally defined as the critical value of the occupation probability p such that infinite connectivity (percolation) first occurs. This definition applies to infinite percolation networks where the infinite connectivity refers to the formation of a single, giant connected component which spans the entire space.

Percolation theory provides several analytical and empirical results for the percolation thresholds of such networks. A simple example is the infinite 2D square lattice. For this lattice the vertices of the squares are the “nodes” and the connections can be formed between a node and any one of its four nearest neighbour nodes (those to the north, east, south and west of the node). The value p is the probability that a randomly chosen pair of nearest

neighbour nodes will be connected by a bond. The percolation threshold for such a network is $p = 0.5$. This means that in an infinite square lattice, if half of all possible bonds between nearest neighbour nodes are occupied (at random) there will be a giant connected component on the lattice.

5 Another theoretical percolation threshold is that for the Delaunay triangulation of a random 2D lattice. A Delaunay triangulation of a random set of points is the triangulation (i.e. the subdivision of the plane into triangles with the points of the random 2D lattice as vertices) such that no point is inside the circumcircle (i.e. the circle defined by the three points of a triangle) of any triangle. Essentially the Delaunay triangulation of a random 2D
10 lattice is just a reasonable model for randomly distributed “pylons” connected by randomly distributed “wires”. In this case the percolation threshold is around $p = 0.33$, meaning that if approximately a third of the possible bonds between points in the triangulation are occupied there would be a giant connected component.

 The percolation threshold is, of course, dependent on the form of the lattice. In the
15 present invention the lattice of conductive nodes is often a random lattice. The morphology of the lattice of conductive nodes can be studied by SEM or AFM.

 The term “percolation region”, as used herein, applies to a finite percolation network comprising conductive nodes and connector molecules disposed between electrodes and refers to such a percolation network wherein the number and configuration of connector
20 molecules between conductive nodes is such that percolation network is between the percolation threshold for a finite network, as described above, and the thin film limit. The percolation region is a region defined by the areal (i.e. by area) concentration of connector molecules. Within the percolation region the value of an electrical property will be critically dependent on the number of connections made by connector molecules between conductive
25 nodes.

 The mid-point of the percolation region is where the electrical property of the percolation network varies most rapidly as a function of the number of connector molecules disposed on the substrate comprising conductive nodes is varied. The point at which the electrical property varies most rapidly as the number of connector molecules increases can be
30 found experimentally by observing the change in the electrical property of the network as more connector molecules are disposed and stopping disposition when the electrical property is varying most rapidly. For example, the disposition of the connector molecules could be

stopped when the rate of change of the electrical property with respect to the change in the number of connector molecules is no longer increasing. The percolation region is the region (as the areal density of connector molecules varies) which contains this mid point and extends to the percolation threshold at the lower end and the thin film limit at the upper end.

5 One way in which the mid-point of the percolation region may be found is to measure an electrical property of the network as connector molecules are disposed on the surface in a test component and then using that data from the test component one may determine how many connector molecules need to be disposed on a fresh substrate to form a percolation network at the desired point in the percolation region.

10 The term “critically dependent”, as used herein, means that changes in electrical connections made by connector molecules between conductive nodes causes a rapid change in an electrical property of the system. In the percolation region the critically dependent property changes rapidly (as the electrical connections change) relative to the same property in the thin film limit (when the electrical connections change by the corresponding amount).

15 The term “rapidly”, as used herein, may refer to a change of an electrical property of a conductive node/connector molecule percolation network in the percolation region which is more than 10% greater, more than 50% greater, or more than 100% greater than the corresponding change in a thin film of the connector molecules. For instance, the change of an electrical property of a conductive node/connector molecule percolation network in the
20 percolation region may be from 10% to 1000% greater than the corresponding change in a thin film of the connector molecules. The term “critically dependent” would be well recognised by the skilled person. The percolation region is shown schematically in Figure 2.

 The term “thin film limit”, as used herein, refers to a percolation network wherein the number of connector molecule is such that the electrical properties of the percolation network
25 are similar to those of a thin film comprising the connector molecules. In the thin film limit the number of connector molecules will be such that there is a significant continuous mass of connector molecules between the two electrodes and the percolation network is replaced by a thin film of connector molecules. In the thin film limit, the conductive node/connector molecule percolation network can appear, when using SEM or AFM, simply as a thin film
30 deposited on the surface of the conductive nodes disposed on an insulating substrate. The upper surface which is exposed to the analyte behaves as a thin film rather than a percolation network.

Usually, the plurality of connector molecules together form a layer on the substrate whose thickness is equal to or less than 200 nm, equal to or less than 100 nm, equal to or less than 60 nm, or equal to or less than 40 nm. Typically, the thickness of the layer of connector molecules is from 0.2 nm to 200 nm, from 0.1 nm to 100 nm, or from 0.5 nm to 40 nm. Preferably, the thickness of the layer of connector molecules is from 1 nm to 10 nm. More preferably, the thickness of the layer of connector molecules is from 2 nm to 5 nm. At these thicknesses of connector molecules, the conductive node/connector molecule percolation network is typically in the percolation region.

Accordingly, the sensor component may comprise:

- (i) a first electrode and a second electrode;
 - (ii) an insulating substrate disposed between the first electrode and the second electrode;
 - (iii) a plurality of conductive nodes disposed on a surface of the insulating substrate; and
 - (iv) a layer of connector molecules of thickness from 0.5 nm to 40 nm, for instance from 1 nm to 10 nm, wherein the connector molecules two or more groups capable of forming a chemical bond with a conductive node or an electrode, and wherein the connector molecules are capable of displaying a change in an electrical property in response to interaction with an analyte;
- wherein at least some of the connector molecules are bonded to one or more nodes, or to one electrode, and electrical junctions are formed between separate nodes or between a node and an electrode; and
- wherein the electrical junctions form an electrical percolation network over the insulating substrate, which electrical percolation network comprises at least one continuous pathway of connector molecules and conductive nodes which connects the first electrode and the second electrode.

Preferably, the thickness of the layer of semiconductor molecules disposed on the substrate comprising conductive nodes is less than the height (maximum thickness) of the conductive nodes. For example, the thickness of the layer of connector may be equal to or less than 100%, equal to or less than 80%, or from 1% to 100%, or from 5% to 80% of the height of the conductive nodes.

The layer of connector molecules formed will not usually comprise a continuous mass of connector molecules between the two electrodes (through which no conductive nodes are exposed), unless the conductive node/connector molecule percolation network is in the thin film limit.

5 The advantage of the present invention lies in the critical behaviour of electrical properties of the conductive node/connector molecule percolation network in the percolation region. The critical dependence corresponds to an extreme sensitivity which allows very low concentrations of analyte to be detected. In the percolation network based sensor of the present invention, the presence of a small number of analyte molecules can change the
10 electrical properties of the same, small number of connector molecules and, due to the properties of a percolation network, alter the large scale electrical properties of the entire network to cause an amplified response. In a thin film electrochemical sensor using the same type of connector molecule, the same, small number of analyte molecules can, again, change the electrical properties of the same, small number of connector molecules but, since these
15 molecules are swamped in a disordered mass of other connector molecules (the thin film), any response is expected to be minor. The sensor components of the invention have the potential to operate at a parts per billion (ppb) sensitivity whereas those of the prior art generally operate at a parts per million (ppm) sensitivity.

 Although it is preferable that the sensor component of the present invention operates
20 within the percolation region, the present sensor component will still demonstrate improved sensitivity for a wide range of amounts of connector molecules, up to and including the thin film limit. The reason for this is that the conductive nodes order the connector molecules and improve their electrical contact. In a standard thin film of a connector molecule such as a conjugated polymer many interactions between molecules will be inefficient side/side
25 interactions and electrical states of the molecules will be strongly perturbed by the field variations arising from the disordered surroundings of each connector molecule. These effects will be lessened in an ordered network such as in the present invention. Many connector molecule/connector molecule connections may be end-to-end with highly conductive materials such as gold in between.

30 By preparing the sensor component in configurations which correspond to different regions of the areal density/electrical property graph as shown in Figure 2, it is possible to optimise the sensor component for different tasks. For example, to optimise the sensor

component for simply detecting the presence of an analyte, it is preferable for the percolation network to be at the centre of the percolation region where an electrical property is most critical to changes in the properties of electrical junctions between nodes (caused by interaction with an analyte). On the other hand, if it is desirable to know whether a higher or lower concentration of the analyte is present it is preferable for the sensor component to be towards the thin film limit where the electrical property will vary more slowly upon interaction with an analyte and can provide an indication of the amount of analyte present.

The electrodes used in the present invention may comprise the same or different materials. The first electrode and the second electrode can independently comprise any suitable material.

In one embodiment, the first electrode and the second electrode independently comprise a metal selected from the elements of groups 3 to 16 of the periodic table of the elements, graphite, a conducting oxide, conducting nitride, conducting carbide or a mixture thereof. The first electrode and the second electrode may for instance independently comprise: platinum, palladium, copper, gold, silver, zinc, indium tin oxide, graphite or a mixture thereof. In one embodiment the first and second electrodes comprise platinum.

Examples of metals selected from groups 3 to 16 of the periodic table of the elements include scandium, yttrium, lanthanum, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, copper, silver, gold, zinc, cadmium, mercury, aluminium, gallium, indium, tin, lead, antimony and bismuth. Examples of conducting oxides include tin oxide (SnO_2), indium oxide (In_2O_3), indium tin oxide (ITO), and zinc oxide (ZnO) all of which can optionally be doped. The electrodes can comprise any of these materials as appropriate. The term “doped”, as used herein, refers to the presence of an impurity element at a concentration ranging between 0.00001 to 40%. If the impurity element acts as an electron donor, then the semiconductor material will be doped to become n-type, if the impurity element acts as an electron acceptor, then the semiconductor material will be doped to become p-type.

The first electrode and the second electrode may be interdigitated. The term “interdigitated”, as used herein, can refer to comb-shaped, interlocking, yet non-contacting, regions and is understood by the skilled person. In some cases interdigitated electrodes may take other forms such as, for example, interlocking spirals.

The sensor component of the present invention may further comprise one or more electrodes other than the first electrode and the second electrode. Thus, in one embodiment, the sensor component comprises one or more further electrodes. The additional electrodes may have a variety of functions. In one embodiment, one or more of the further electrodes
5 operates as a back-gate.

Connections between the electrode and the conductive node/connector molecule percolation network may be formed through a connector molecule bonded through one group to a conductive node and another group to an electrode, or through direct contact between a conductive node and an electrode.

10 The insulating substrate used in the present invention may be any suitable substance with a high resistivity relative to the electrodes. These may include any solid state material with a resistivity of greater than 10 kΩm at 20°C and standard pressure. Such materials include inorganic compounds such as metal oxides, halides, and chalcogenides, and organic compounds such as polyethenes, polyesters and other non-conducting polymers. The
15 insulating substrate may for instance comprise magnesium oxide, strontium titanate, beryllium oxide, aluminium oxide, aluminium nitride, silicon dioxide or a mixture thereof. The insulating substrate may comprise greater than 95% by weight of magnesium oxide, strontium titanate, beryllium oxide, aluminium oxide, aluminium nitride or silicon dioxide. In one embodiment, the insulating substrate is in the form of a single crystal. The insulating
20 substrate may for instance be a single crystal of magnesium oxide, strontium titanate, beryllium oxide, aluminium oxide, aluminium nitride or silicon dioxide. The insulating substrate is preferably a MgO (001) single crystal.

The two components of the percolation network disposed between the first and second electrodes used in the sensor component of the present invention are the conductive nodes
25 and the connector molecules. As described above, the conductive nodes act as the lattice points in the electrical percolation network between which connector molecules may form connections. When there is a certain number of connector molecules forming connections between conductive nodes (and between conductive nodes and the electrodes) in the electrical percolation network, the electrical percolation network is in what is known as the percolation
30 region, as described above. In this region, electrical properties of the network depend critically on the number of connections in the network.

The connector molecules used in the invention comprise two or more groups capable of forming chemical bonds with a node or an electrode. The connector molecules must in some way display a change in an electrical property of the molecule on interaction with an analyte. It is this change in an electrical property which either “switches on” (for example by increasing the conductivity or another electrical property of the connector molecule) or “switches off” (for example by decreasing the conductivity or another electrical property of the connector molecule) the connector molecules and changes the connectivity of the conductive node/connector molecule percolation network. If the percolation network is in the percolation region, the change in connectivity will cause a rapid, critical change in an electrical property of the network. The advantage over thin film sensor components is that this rapid, critical change will be far easier to detect as discussed above. The conductive nodes and connector molecules suitable for use in the invention are described below.

The conductive nodes disposed on the surface of the insulating substrate in the present invention can comprise any suitable electrically conductive material. In one embodiment, the conductive nodes comprise a metal selected from groups 3 to 16 of the periodic table of the elements, a conducting oxide, a conducting nitride, a conducting carbide, a conducting organic material or a mixture thereof. Conducting organic materials include doped conducting organic materials. In one embodiment, the conductive nodes comprise gold, silver, platinum, palladium, iridium, copper, tungsten (IV) oxide, iron (II, III) oxide or a mixture thereof. In a preferred embodiment, the conductive nodes comprise gold.

Examples of metals selected from groups 3 to 16 of the periodic table of the elements include scandium, yttrium, lanthanum, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, copper, silver, gold, zinc, cadmium, mercury, aluminium, gallium, indium, tin, lead, antimony and bismuth. Examples of conducting oxides include tin oxide (SnO_2), indium oxide (In_2O_3), indium tin oxide (ITO), and zinc oxide (ZnO) all of which can optionally be doped. Examples of conductive organic materials include doped polyacetylene and other doped conductive polymers. The conductive nodes can comprise any of these materials.

The conductive nodes disposed on the surface of the insulating substrate may have any shape. The conductive nodes may themselves be interdigitated. The conductive nodes must be isolated so that no current may bridge the gap between them and so that they act as

“pylons” for the “wires” formed of the connector molecules. Some gaps between conductive nodes must be small enough so that connector molecules may form chemical bonds with each of the conductive nodes and form an electrical junction between them. The conductive nodes can be amorphous or crystalline.

5 The height (maximum thickness) of a conductive node may be defined as the distance between the surface of the insulating substrate on which the node is disposed and the upper surface of the node. Usually, the height of the conductive nodes disposed on the surface of the insulating substrate, is equal to or less than 500 nm. Typically, the height of the conductive nodes is from 0.3 nm to 200 nm. The height may for instance be from 5 nm to 100
10 nm, or preferably from 20 nm to 40 nm.

Typically, the size of a conductive node that is disposed on the surface of the insulating substrate, is from 1 nm to 5000 nm, or from 1 nm to 2000 nm. Usually, size is from 10 nm to 500 nm, or from 15 nm to 150 nm. The size of a node is, if the node is circular, the diameter of the node (measured parallel to the surface of the substrate), or, if the
15 node is not circular, the diameter of a circular node occupying the same area on the substrate (measured parallel to the surface of the substrate).

The distance between any two adjacent nodes is typically from 0.1 nm to 100 nm or from 0.5 nm to 50 nm. Usually, the distance between two adjacent nodes is from 5 nm to 10 nm.

20 The height, size and distance between the nodes can all be measure by scanning electron microscopy (SEM) or atomic force microscopy (AFM).

The connector molecules are the analyte-sensitive elements of the sensor component provided by the present invention. Accordingly, the connector molecules must display a change in an electrical property in response to interaction with an analyte. This change may
25 be caused by any mechanism. Possible mechanisms include the formation of a chemical bond or bonds between the analyte and the connector molecule, the transfer of an electron between the analyte and the connector molecule (in either direction, sometimes forming an acceptor/donor complex), the transfer of a proton or another chemical group between the analyte and the connector molecule (in either direction), or a conformational change in the
30 structure of connector molecule on interaction with the analyte. All of these mechanisms can

cause a change in an electrical property of the connector molecule of varying magnitude. The sensitivity of a percolation network allows even minor changes to be detected.

The connector molecule can be any suitable molecule comprising two or more groups capable of forming chemical bonds with a conductive node, or with either a conductive node
5 or an electrode, wherein the connector molecule is capable of displaying a change in an electrical property in response to interaction with an analyte. The connector molecule will typically be an electrically conducting molecule.

The connector molecules may form junctions between two adjacent nodes. At least some of the connector molecules are bonded to one or more nodes, or to one electrode, and
10 electrical junctions are formed between separate nodes or between a node and an electrode. Here, "some", means more than one. Typically, the junction will be formed of one or more connector molecules lying between the two nodes. For example, a node may be bonded or bound to a connector molecule which is then bound (through any kind of interaction) to a second connector molecule which is itself bonded to a second node. The connection here
15 thus has the form N-CM-CM-N, where N means node, and CM means connector molecule. Alternatively, there may be more than two connector molecules in sequence between two nodes, for example N-CM-CM-CM-N. There may be three or more connector molecules between two adjacent nodes. Preferably, at least some of the connector molecules are bonded to two or more nodes, or to one electrode and one or more nodes, and form electrical
20 junctions between separate nodes or between a node and an electrode. In this case, the junction between the nodes is may be formed by a single connector molecules which is bonded through separate groups to two adjacent nodes.

In one embodiment, the connector molecules comprise conjugated molecules. The term "conjugated", as used herein, refers to molecules comprising a delocalised system of π -
25 electrons. Conjugated molecules will generally have higher electron mobility than non-conjugated molecules. However, non-conjugated molecules can still display detectable changes in an electrical property on interaction with an analyte.

In one embodiment, the connector molecules comprise conjugated oligomers or polymers or a mixture thereof. The terms "oligomers" and "polymers", as used herein, refer
30 to molecules comprising one or more types of repeating units. Typically, an oligomer will comprise from 2 to 10 repeating units. Dimers, trimers and tetramers are examples of oligomers. Polymers typically comprise more than 10 repeating units.

There are a large number of different types of conjugated polymers or oligomers. Conjugated polymers and oligomers in general are useful as connector molecules in the sensor component of the invention as they all comprise extended delocalised systems of electrons that can be interrupted or enhanced through interaction with an analyte. Conjugated
5 oligomers and polymers can comprise repeating units comprising arylene, heteroarylene, alkenylene (e.g. C₁₋₂₀ alkenylene) or alkynylene (e.g. C₁₋₂₀ alkynylene) units. Conjugated oligomers and polymers can additionally or alternatively comprise alkenyl (e.g. C₁₋₂₀ alkenyl), alkynyl (e.g. C₁₋₂₀ alkynyl), aryl or heteroaryl groups.

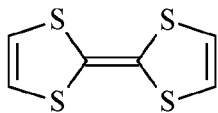
In one embodiment, the connector molecules are selected from polyacetylenes,
10 polyphenylenes, polyparaphenylenes, polyparaphenylene vinylenes, polyparaphenylene acetylenes, polyazulenes, polynaphthalenes, polypyrenes, polyanilines, polyparaphenylene sulphides, polyfluorenes, polypyrroles, polythiophenes, polythieno[3,2-b]thiophene, polycarbazoles, polyazepines and polyindoles or a mixture thereof. The term “mixtures thereof”, as used in the context of conjugated polymers and oligomers herein, refers to
15 conjugated polymers or oligomers comprising repeating units selected from one or more of the conjugated polymers listed. Such a polymer or oligomer could comprise alternating repeating units of phenylene and thiophene for example. Such polymers are known as co-polymers. The connector molecules are optionally selected from polyanilines, polythiophenes, polyparaphenylenes and polypyrrolles. The conjugated polymers or
20 oligomers can be derivatives of the base polymer. Therefore, polyacetylenes include derivatives of the base polymer polyacetylene and polythiophenes include derivatives of the base polymer polythiophene. The term “derivative”, as used herein, refers to molecules which have been functionalised by other chemical groups.

For example, polythiophenes include poly(alkylthiophenes) and other substituted
25 polythiophenes. The connector molecules may, for example, be poly(3-hexylthiophene) or poly(3,4-ethylenedioxythiophene).

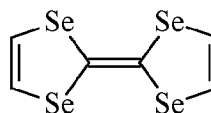
The connector molecules can be polymers or oligomers of thiophene. Optionally the connector molecules are di-, tri-, tetra-, penta- or sexithiophene or their derivatives. The connector molecules may, for instance, be sexithiophene or substituted sexithiophene.

30 Polymers and oligomers used as connector molecules do not have to be linear. They can also be dendritic oligomers or polymers. Dendritic oligomers are examples of connector molecules that can form connections between more than two nodes.

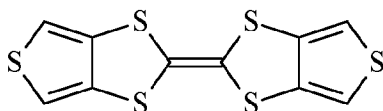
The connector molecules can be small monomeric or dimeric conjugated molecules. In one embodiment, the connector molecules are selected from tetrathiafulvalene (formula I), tetraselenafulvalene (formula II), dithiophene-tetrafulvalene (formula III), tetrathiatetracene (formula IV), N,N,N', N'-tetramethyl-phenylenediamine (formula V) and trimethoxybenzene (formula VI) or a mixture thereof. The derivatives of each of these molecules can also be used.



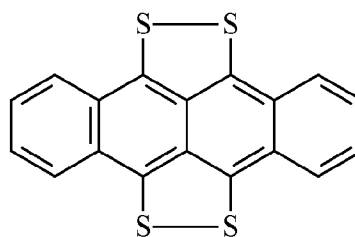
I



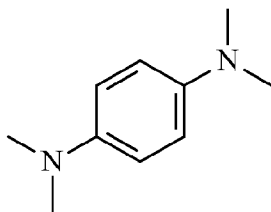
II



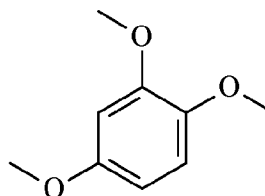
III



IV



V



VI

The connector molecules of the invention may in some embodiments comprise a metal complex. The connector molecules can also comprise other conjugated molecules such as porphyrins.

The connector molecules may be carbon nanotubes, whether they are single-walled or multi-walled.

The connector molecules may be unsubstituted or substituted.

When a connector molecule is substituted it typically bears one or more substituents (for instance 1, 2 or 3 substituents) selected from: substituted or unsubstituted C₁₋₂₀ alkyl, substituted or unsubstituted C₂₋₂₀ alkenyl, substituted or unsubstituted C₂₋₂₀ alkynyl,

substituted or unsubstituted aryl (as defined herein), substituted or unsubstituted heteroaryl, cyano, amino, C₁-C₁₀ alkylamino, di(C₁-C₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acylamido, hydroxy, oxo, halo, carboxy, ester, acyl, acyloxy, C₁-C₂₀ alkoxy, aryloxy, haloalkyl, sulfonic acid, sulfhydryl (i.e. thiol, -SH), C₁-C₁₀ alkylthio, 5 arylthio, sulfonyl, phosphoric acid, phosphate ester, phosphonic acid and phosphonate ester. Examples of substituted alkyl groups include haloalkyl, hydroxyalkyl, aminoalkyl, alkoxyalkyl and alkaryl groups. The term alkaryl, as used herein, pertains to a C₁-C₂₀ alkyl group in which at least one hydrogen atom has been replaced with an aryl group. Examples of such groups include, but are not limited to, phenyl, benzyl (phenylmethyl, PhCH₂-), 10 benzhydryl (Ph₂CH-), trityl (triphenylmethyl, Ph₃C-), phenethyl (phenylethyl, Ph-CH₂CH₂-), styryl (Ph-CH=CH-) and cinnamyl (Ph-CH=CH-CH₂-).

Typically a substituted alkyl group carries 1, 2 or 3 substituents, for instance 1 or 2. The substituents may be selected from those defined above.

An aryl group is a substituted or unsubstituted, monocyclic, bicyclic, tricyclic or 15 polycyclic aromatic group which typically contains from 6 to 18 carbon atoms in the ring portion. Examples include phenyl, naphthyl, anthracyl, pyrenyl, indenyl and indanyl groups. An aryl group is unsubstituted or substituted. When an aryl group as defined above is substituted it typically bears one or more substituents selected from C₁-C₆ alkyl which is unsubstituted (to form an aralkyl group), aryl which is unsubstituted, cyano, amino, C₁-C₁₀ 20 alkylamino, di(C₁-C₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acylamido, hydroxy, halo, carboxy, ester, acyl, acyloxy, C₁-C₂₀ alkoxy, aryloxy, haloalkyl, sulfhydryl (i.e. thiol, -SH), C₁-C₁₀ alkylthio, arylthio, sulfonic acid, phosphoric acid, phosphate ester, phosphonic acid and phosphonate ester and sulfonyl. Typically it carries 0, 1, 2 or 3 substituents. A substituted aryl group may be substituted in two positions with a single C₁-C₆ 25 alkylene group, or with a bidentate group represented by the formula -X-(C₁-C₆)alkylene, or -X-(C₁-C₆)alkylene-X-, wherein X is selected from O, S and NR, and wherein R is H, aryl or C₁-C₆ alkyl. Thus a substituted aryl group may be an aryl group fused with a cycloalkyl group or with a heterocyclyl group. The ring atoms of an aryl group may include one or more heteroatoms (as in a heteroaryl group). Such an aryl group (a heteroaryl group) is a 30 substituted or unsubstituted monocyclic, bicyclic, tricyclic or polycyclic heteroaromatic group which typically contains from 6 to 18 atoms in the ring portion including one or more heteroatoms. It is generally a 5- or 6-membered ring, containing at least one heteroatom selected from O, S, N, P, Se and Si. It may contain, for example, 1, 2 or 3 heteroatoms.

Examples of heteroaryl groups include pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl, furanyl, thienyl (i.e. thiophenyl), pyrazolidinyl, pyrrolyl, oxazolyl, oxadiazolyl, isoxazolyl, thiadiazolyl, thiazolyl, isothiazolyl, imidazolyl, pyrazolyl, quinolyl and isoquinolyl. A heteroaryl group may be unsubstituted or substituted, for instance, as specified above for aryl.

5 Typically it carries 0, 1, 2 or 3 substituents.

An arylene group is an unsubstituted or substituted bidentate moiety obtained by removing two hydrogen atoms, one from each of two different aromatic ring atoms of an aromatic compound, which moiety has from 5 to 14 ring atoms (unless otherwise specified). Typically, each ring has from 5 to 7 or from 5 to 6 ring atoms. An arylene group may be
10 unsubstituted or substituted, for instance, as specified above for aryl. Typically a substituted heteroarylene group carries 1, 2 or 3 substituents, for instance 1 or 2.

In this context, the prefixes (e.g., C₅₋₂₀, C₆₋₂₀, C₅₋₁₄, C₅₋₇, C₅₋₆, etc.) denote the number of ring atoms, or range of number of ring atoms, whether carbon atoms or heteroatoms. For example, the term "C₅₋₆ arylene," as used herein, pertains to an arylene group having 5 or 6
15 ring atoms. Examples of groups of arylene groups include C₅₋₂₀ arylene, C₆₋₂₀ arylene, C₅₋₁₄ arylene, C₆₋₁₄ arylene, C₆₋₁₀ arylene, C₅₋₁₂ arylene, C₅₋₁₀ arylene, C₅₋₇ arylene, C₅₋₆ arylene, C₅ arylene, and C₆ arylene.

The ring atoms may be all carbon atoms, as in "carboarylene groups" (e.g., C₆₋₂₀ carboarylene, C₆₋₁₄ carboarylene or C₆₋₁₀ carboarylene).

20 Examples of C₆₋₂₀ arylene groups which do not have ring heteroatoms (i.e., C₆₋₂₀ carboarylene groups) include, but are not limited to, those derived from the compounds discussed above in regard to aryl groups, e.g. phenylene, and also include those derived from aryl groups which are bonded together, e.g. phenylene-phenylene (diphenylene) and phenylene-phenylene-phenylene (triphenylene).

25 Alternatively, the ring atoms may include one or more heteroatoms, as in "heteroarylene groups" (e.g., C₅₋₁₀ heteroarylene). A heteroarylene group may be unsubstituted or substituted, for instance, as specified above for aryl. Typically a substituted heteroarylene group carries 1, 2 or 3 substituents, for instance 1 or 2.

30 Examples of heteroarylene groups include, but are not limited to, those derived from the compounds discussed above in regard to heteroaryl groups. Examples of heteroarylene groups include bidentate groups derived from pyridine, pyrazine, pyrimidine, pyridazine, furan, thiofuran (i.e. thiophene), pyrazole, pyrrole, oxazole, oxadiazole, isoxazole, thiadiazole, thiazole, isothiazole, imidazole and pyrazole.

An alkenyl group is a straight or branched group, which, unless otherwise specified, contains from 2 to 20 carbon atoms (i.e. a C₂₋₂₀ alkenyl group). One or more double bonds may be present in the alkenyl group, typically one double bond. A C₂₋₂₀ alkenyl group is typically ethenyl or a C₃₋₁₀ alkenyl group, i.e. a C₂₋₁₀ alkenyl group, more typically a C₂₋₆ alkenyl group. A C₃₋₁₀ alkenyl group is typically a C₃₋₆ alkenyl group, for example allyl, propenyl, butenyl, pentenyl or hexenyl. A C₂₋₄ alkenyl group is ethenyl, propenyl or butenyl. An alkenyl group may be unsubstituted or substituted by one to four (e.g. one, two, three or four) substituents, the substituents, unless otherwise specified, being selected from those listed above for C₁₋₂₀ alkyl groups. Where two or more substituents are present, these may be the same or different.

An alkynyl group is a straight or branched group which, unless otherwise specified, contains from 2 to 20 carbon atoms (i.e. a C₂₋₂₀ alkynyl group). One or more triple bonds, and optionally one or more double bonds may be present in the alkynyl group, typically one triple bond. A C₂₋₂₀ alkynyl group is typically ethynyl or a C₃₋₁₀ alkynyl group, i.e. a C₂₋₁₀ alkynyl group, more typically a C₂₋₆ alkynyl group. A C₃₋₁₀ alkynyl group is typically a C₃₋₆ alkynyl group, for example propynyl, butynyl, pentynyl or hexynyl. A C₂₋₄ alkynyl group is ethynyl, propynyl or butynyl. An alkynyl group may be unsubstituted or substituted by one to four substituents (e.g. one, two, three or four), the substituents, unless otherwise specified, being selected from those listed above for aryl groups. Where two or more substituents are present, these may be the same or different.

An alkylene group is an unsubstituted or substituted bidentate moiety obtained by removing two hydrogen atoms, either both from the same carbon atom, or one from each of two different carbon atoms, of a hydrocarbon compound having from 1 to 20 carbon atoms (i.e. C₁₋₂₀ alkylene) unless otherwise specified, which may be aliphatic or alicyclic, and which may be saturated, partially unsaturated, or fully unsaturated. Thus, the term "alkylene" includes the sub-classes alkenylene (C₁₋₂₀ alkenylene), alkynylene (C₁₋₂₀ alkynylene), cycloalkylene, etc. Typically it is C₁₋₁₀ alkylene, or C₁₋₆ alkylene. Typically it is C₁₋₄ alkylene, for example methylene, ethylene, i-propylene, n-propylene, t-butylene, s-butylene or n-butylene. It may also be pentylene, hexylene, heptylene, octylene and the various branched chain isomers thereof. An alkylene group may be unsubstituted or substituted, for instance, as specified above for alkyl. Typically a substituted alkylene group carries 1, 2 or 3 substituents, for instance 1 or 2.

In this context, the prefixes (e.g., C₁₋₄, C₁₋₇, C₁₋₁₀, C₂₋₇, C₃₋₇, etc.) denote the number of carbon atoms, or range of number of carbon atoms. For example, the term "C₁₋₄alkylene," as

used herein, pertains to an alkylene group having from 1 to 4 carbon atoms. Examples of groups of alkylene groups include C₁₋₄ alkylene ("lower alkylene"), C₁₋₇ alkylene and C₁₋₁₀ alkylene.

Examples of linear saturated C₁₋₇ alkylene groups include, but are not limited to, 5 -(CH₂)_n- where n is an integer from 1 to 7, for example, -CH₂- (methylene), -CH₂CH₂- (ethylene), -CH₂CH₂CH₂- (propylene), and -CH₂CH₂CH₂CH₂- (butylene).

Examples of branched saturated C₁₋₇ alkylene groups include, but are not limited to, -CH(CH₃)-, -CH(CH₃)CH₂-, -CH(CH₃)CH₂CH₂-, -CH(CH₃)CH₂CH₂CH₂-, -CH₂CH(CH₃)CH₂-, -CH₂CH(CH₃)CH₂CH₂-, -CH(CH₂CH₃)-, -CH(CH₂CH₃)CH₂-, and 10 -CH₂CH(CH₂CH₃)CH₂-.

Examples of linear partially unsaturated C₁₋₇ alkylene groups (C₁₋₇ alkenylene groups) include, but are not limited to, -CH=CH- (vinylene), -CH=CH-CH₂-, -CH₂-CH=CH₂-, -CH=CH-CH₂-CH₂-, -CH=CH-CH₂-CH₂-CH₂-, -CH=CH-CH=CH-, -CH=CH-CH=CH-CH₂-, -CH=CH-CH=CH-CH₂-CH₂-, -CH=CH-CH₂-CH=CH-, and -CH=CH-CH₂-CH₂-CH=CH-.

15 Examples of branched partially unsaturated C₁₋₇ alkylene groups (C₁₋₇ alkenylene groups) include, but are not limited to, -C(CH₃)=CH-, -C(CH₃)=CH-CH₂-, and -CH=CH-CH(CH₃)-.

Examples of alicyclic saturated C₁₋₇ alkylene groups include, but are not limited to, cyclopentylene (e.g., cyclopent-1,3-ylene), and cyclohexylene (e.g., cyclohex-1,4-ylene).

20 Examples of alicyclic partially unsaturated C₁₋₇ alkylene groups (cyclic C₁₋₇ alkenylene groups) include, but are not limited to, cyclopentenylene (e.g., 4-cyclopenten-1,3-ylene), cyclohexenylene (e.g., 2-cyclohexen-1,4-ylene; 3-cyclohexen-1,2-ylene; 2,5-cyclohexadien-1,4-ylene). These are examples of C₅₋₆ cycloalkylene groups.

Optionally, the connector molecules may be doped with another substance. For 25 example, the dopant may be an element, an organic acid or a mineral acid. Examples of doped connector molecules (here, conductive polymers), are given in the following table:

Conductive polymers	Dopant	Analyte species
Polyaniline	Small inorganic ions	ammonia
	Acrylic acid	ammonia
	Camphosphonic acid	water
Polypyrrole	Naphthalene sulfonic acid	acetone
	Camphor sulfonic acid	acetone
	Tannic acid	dopamine
Polythiophene	Hydrolyzed fluoroalkyl trichlorosilane	acetone, water, and hexane

Doping may occur before or after the connector molecules are disposed on the surface comprising the conductive nodes. This table also provides examples of analytes which may be detected by each of the given doped connector molecules.

Conjugated molecules used in electrochemical sensors can be tailored to respond to specific analytes by attaching analyte-specific pendant groups to the main chain of the polymer. The pendant groups can show very high specificity for certain compounds. Some such groups are described in McQuage *et al.*, "Conjugated Polymer-Based Chemical Sensors," *Chem. Rev.*, 100, 2537-2574 (2000). Examples include crown-ethers for detecting ions, pyridyl based groups for detecting metals, and antibodies for biological molecules. For the detection of electron poor molecules such as nitro-based explosives, electron donor groups can be used as pendant groups. Specificity for particular electron poor molecules could be tuned by selecting electron donor groups where the electron transfer between the two will be resonant (resonance electron transfer).

The pendant group does not have to be bonded directly to the backbone of the connector molecule, as changes in the pendant group on interaction with an analyte can affect the connector molecule through bonds or via a through-space interaction.

Thus, the connector molecules may comprise a pendant group, A, which is selective for an analyte.

In some embodiments, the connector molecules are substituted with one or more groups of formula $-X-A$, wherein X is a bond or a unsubstituted or substituted C_{1-10} alkylene group and A is a pendant group selective for an analyte. The alkylene group may be as defined above. When X is a bond, it may be a single, double or triple bond.

The pendant group A may for instance be an amine, an ester, a crown-ether, a cryptand, C_1-C_{30} aryl, C_1-C_{30} heteroaryl, a fullerene, iptycene, cyclodextrin, calixerene, a metallocene, an enzyme or an antibody.

The term "crown ether", as used herein, refers to monocyclic chemical compounds that comprise several ether groups. Examples of crown ethers include 12-crown-4, 15-crown-5, 18-crown-6, dibenzo-18-crown-6, and diaza-18-crown-6. Crown ethers may be substituted. The term "cryptand", as used herein, refers to bi- or polycyclic, polydentate chemical compounds containing several ether groups and at least one tertiary amine group. An example of a cryptand is [2.2.2]-cryptand (1,10-diaza-4,7,13,16,21,24-

hexaoxabicyclo[8.8.8]hexacosane). Aryl and heteroaryl are as defined above. The term “iptycene”, as used herein, refers to a chemical compound wherein a number of arene units are joined together to form the bridges of [2.2.2] bicyclic ring system. Examples of iptycenes include triptycene (9,10-o-Benzeno-9,10-dihydroanthracene). The term “cyclodextrin”, as used herein, refers to cyclic compounds comprising sugar molecules. Example of cyclodextrins include α -, β -, and γ -cyclodextrin. The term “calixerene”, as used herein, refers to is a macrocycle or cyclic oligomer based on a hydroxyalkylation product of a phenol and an aldehyde. The term “metallocene”, as used herein, refers to an organometallic compound comprising two or more aromatic ring ligands bound to a central metal atom.

The connector molecules used in the invention may also form conducting polymer composites. This may be done by disposing connector molecules together with another component. The composite will comprise a connector molecule as defined above and another component which will typically be an insulating polymer, carbon nanotubes, metal clusters or metal oxides. These can enhance sensitivity through, amongst others, electron/proton transfer. Examples of composites are given in “Gas Sensors Based on Conducting Polymers,” Hua Bai and Gaoquan Shi, *Sensors* **2007**, 7, 267-307. Accordingly, the connector molecules may be disposed to form a composite comprising a polymer selected from PPy, PAni or PTh and a second component selected from PS, High density polyethylene (HDPE), PEO, PVA, PMMA, Poly(etheretherketone) (PEEK), PVDF, PVAc, PVC, Poly(acrylonitrile-cobutadiene-co-stryrene) (ABS), Polyurethane (PU), polyimide (PI), PEDOT, poly(butyl butyl acrylate-co-vinyl acetate), EVA/CoPA, C₆₀, SWNT, MWNT, MWNC, carbon black, 4-t-butyl-Cu-phthalocyanine, Nafion®/metal Coated, nylon-6, PEDOT, Calixarene, Pb-phthalocyanine, Cu(II) exchanged hectorite, zeolite and Cu²⁺, Cu, Pd, CuCl₂, CeO₂, In₂O₃, PtO₂, TiO₂, SnO₂, Fe₂O₃, MoO₃, ZnO₂ or WO₃. The composite may be a blend composite or a coated composite. The second component may be deposited before, after or together with the polymer component.

It may be preferred that the connector molecules used in the invention are able to bind to the conductive nodes with a low electrical contact resistance. This is achieved by groups in the connector molecules forming a chemical bond with the conductive nodes. The connector molecules comprise groups capable of forming bonds with a material comprised in the conductive nodes. These groups may be terminal groups or groups in the central moiety of the molecule. These groups may also improve connections between connector molecules, for example, as in the connection N-CM-CM-N described above.

In one embodiment, the connector molecules comprise two groups capable of forming chemical bonds with a conductive node or an electrode and are linear. The two groups capable of forming chemical bonds with a conductive node or an electrode are typically at opposite ends of the linear molecule.

5 The groups capable of forming chemical bonds with a conductive node or either a conductive node and an electrode can be any suitable groups. In one embodiment, the groups capable of forming chemical bonds with a conductive node or either a conductive node and an electrode are independently selected from sulfur containing groups (thiol, disulfide, thioether, thioester, sulfoxide, sulfone, thiosulfinate, sulfimine, sulfoximine, sulfonamide, 10 sulfonediimine, thioketone and thioaldehyde), selenium containing groups (selenol, selenide, diselenide and selenoxide), nitrogen containing groups (amine, amide, imine, imide, nitrile and nitrate), oxygen containing groups (hydroxyl, ketone, aldehyde, acetal, carboxylic acid, ester and ether), phosphorus containing groups (phosphines, phosphates, phosphite, phosphonite and phosphinite) and carbon containing groups (alkenyl and alkynyl). The 15 sulfur containing groups thiol, disulfide, thioether, thioester, sulfoxide, sulfone, thiosulfinate, sulfimine, sulfoximine, sulfonamide, sulfonediimine, thioketone and thioaldehyde have the formulae -SH, -SSR, -SR, -C(O)SR, -S(O)R, -S(O)(O)R, -S(O)SR, -S(=NR')R, -S(O)(=NR')R, -S(O)(O)-NRR', -S(=NR')=NR, -C(S)R and -C(S)H respectively. The selenium containing groups selenol, selenide, diselenide and selenoxide have the formulae - 20 SeH, -SeR, -SeSeR and -Se(O)R respectively. The nitrogen containing groups amine, amide, imine, imide, nitrile and nitrate have the formulae -NRR', -C(O)NRR', -C(=NR')R, -C(O)N(R')C(O)R, -CN and -NO₂ respectively. The oxygen containing groups hydroxyl, ketone, aldehyde, carboxylic acid, ester and ether have the formulae -OH, -C(O)R, -C(O)H, -C(O)OH, -C(O)OR and -OR respectively. The phosphorus containing groups phosphine, 25 phosphate, phosphite, phosphonite and phosphinite have the formulae -P(R')R, -OP(O)(OR')OR, -OP(OR')OR, -P(OR')OR and -P(R')OR respectively. The carbon containing groups alkene and alkyne have the formulae -C(R'')=C(R')R and -C≡CR respectively.

30 R, R' and R'' are substituents which may be themselves connected to the connector molecules (therefore forming a cyclic group). R, R' and R'' may be selected from substituted or unsubstituted C₁₋₂₀ alkyl, substituted or unsubstituted aryl (as defined herein), cyano, amino, C₁₋₁₀ alkylamino, di(C₁-C₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acylamido, hydroxy, oxo, halo, carboxy, ester, acyl, acyloxy, C₁-C₂₀ alkoxy, aryloxy,

haloalkyl, sulfonic acid, sulfhydryl (i.e. thiol, -SH), C₁-C₁₀ alkylthio, arylthio, sulfonyl, phosphoric acid, phosphate ester, phosphonic acid and phosphonate ester.

Sulfur containing groups are known to form strong bonds with some metals. In one embodiment, the groups capable of forming chemical bonds with a conductive node or either
5 a node or an electrode are independently selected from thiol, disulfide, thioether, thioester, sulfoxide, sulfone, thiosulfinate, sulfinimine, sulfoximine, sulfonamide, sulfonediimine, thioketone and thioaldehyde. Of these, thiol and thioether are preferable. An example of a moiety comprising a thioether group is thiophene (thiophenes are a special class of thioether-containing heterocyclic compounds).

10 In one embodiment, the groups capable of forming chemical bonds with a conductive node or an electrode are thiophene groups.

Sulfur forms particularly strong bonds with the surface of metallic gold. In one preferred embodiment of the invention, therefore, the conductive nodes comprise gold and the connector molecules comprise two or more groups comprising a sulphur atom.

15 In a conductive node/connector molecule percolation network where the conductive nodes comprise gold and the connector molecules comprise two or more groups containing sulfur, a particular benefit arises as sulfur containing molecules are known to self assemble on gold surfaces. This leads to a more ordered, and correspondingly more sensitive, electrochemical percolation network. Self-assembly can occur with other combinations of
20 node material and connector molecule substituent.

When the conductive node/connector molecule percolation network in the sensor component of the invention is formed it is required that some connector molecules form connections between nodes. However, some connector molecules may be deposited solely on the surface of a single conductive node, or on the surface of the insulating substrate, and do
25 not therefore take part in the percolation network. Groups and node materials with stronger affinities for each other will reduce the number of such "wasted" connector molecules.

If the connector molecule is a conjugated molecule, the groups bound to the nodes are preferably bound directly to the conjugated moiety of the connector molecule in order to improve the electrical junction between the two nodes connected by the one or more
30 connector molecules. In one embodiment, the groups capable of forming chemical bonds with a conductive node or either a conductive node or an electrode are directly bonded to the

conjugated moiety of the connector molecule, provided the connector molecule comprises a conjugated moiety.

In one embodiment, the bonds between the connector molecules and the nodes or the electrodes are covalent or ionic. The terms “covalent” and “ionic”, as used herein concerning bonding, refers to the two extremes of charge and electron transfer between the two atoms bound. In a pure covalent bond, there is no charge transfer and bonding electrons are shared equally by each atom. In a pure ionic bond there is a complete transfer of one or more electrons from one atom to another and the corresponding charge transfer. Both of these extremes of bonding, and their intermediate forms, allow for good electrical contact between a connector molecule and a node.

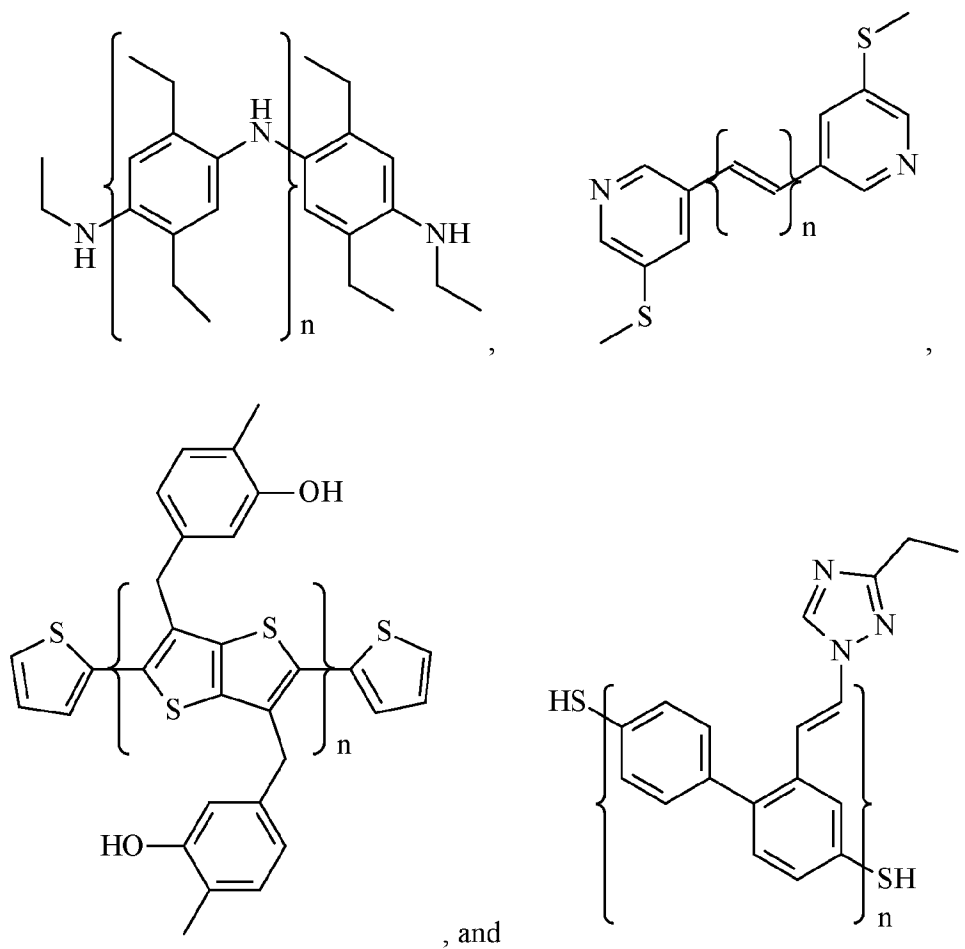
One or more different connector molecules may be present in the sensor component of the invention. Different connector molecules may be sensitive to different analytes.

The connector molecules used in the invention display a change in an electrical property on interaction with an analyte. Most molecules will display some form of change in energy upon interaction with a wide range of analytes. Electrical properties include resistivity (conductivity), capacitance, permeability, permittivity, magneto-resistance or dielectric strength. Conductance and resistivity are directly inversely related and, accordingly, when reference is made to a “change in resistivity” an implicit reference is made to an (inverse) “change in conductivity”. The terms “electrical property” and “electrical properties”, as used herein in the context of connector molecules, refer to macroscopic electric properties of the connector molecules in a bulk phase.

In some embodiments, the electrical property of the connector molecules which changes in response to interaction with an analyte is resistance, impedance, capacitance, permeability, permittivity, magneto-resistance or dielectric strength. More typically, the electrical property of the connector molecules which changes in response to interaction with an analyte is resistance (or conductance), impedance, or capacitance. For example, the electrical property is resistance or conductance.

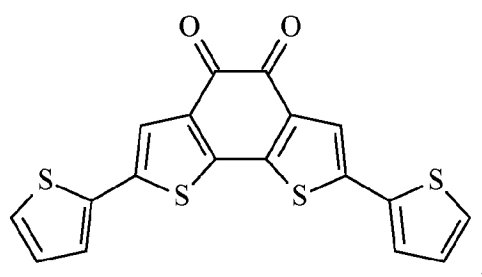
There are a huge range of possible connector molecules. A few representative examples are now presented.

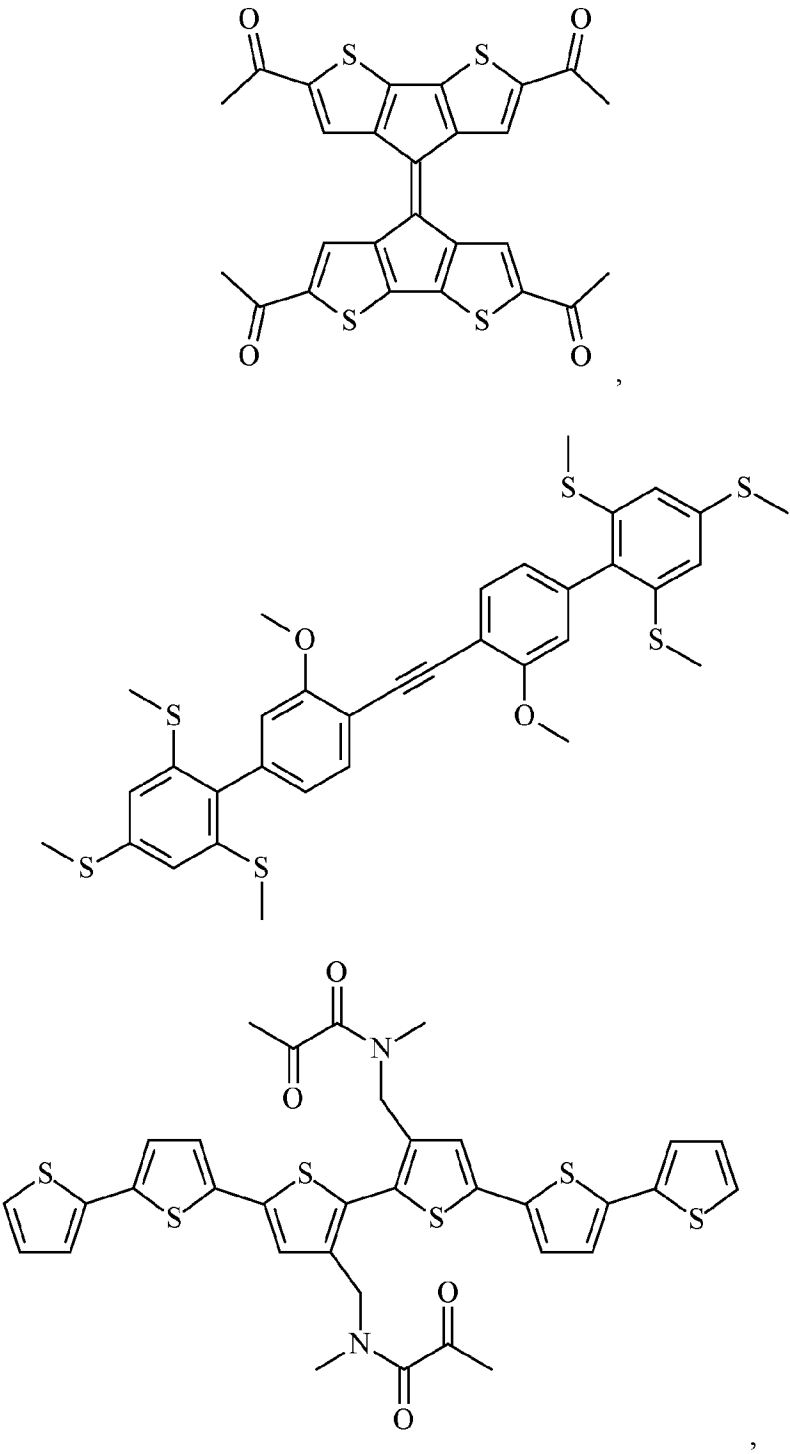
Examples of conjugated polymer connector molecules include:

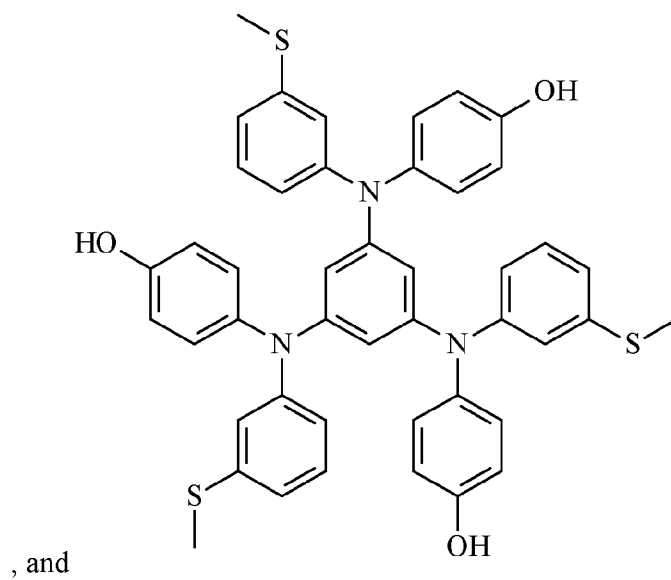


where n is an integer between 3 and 20.

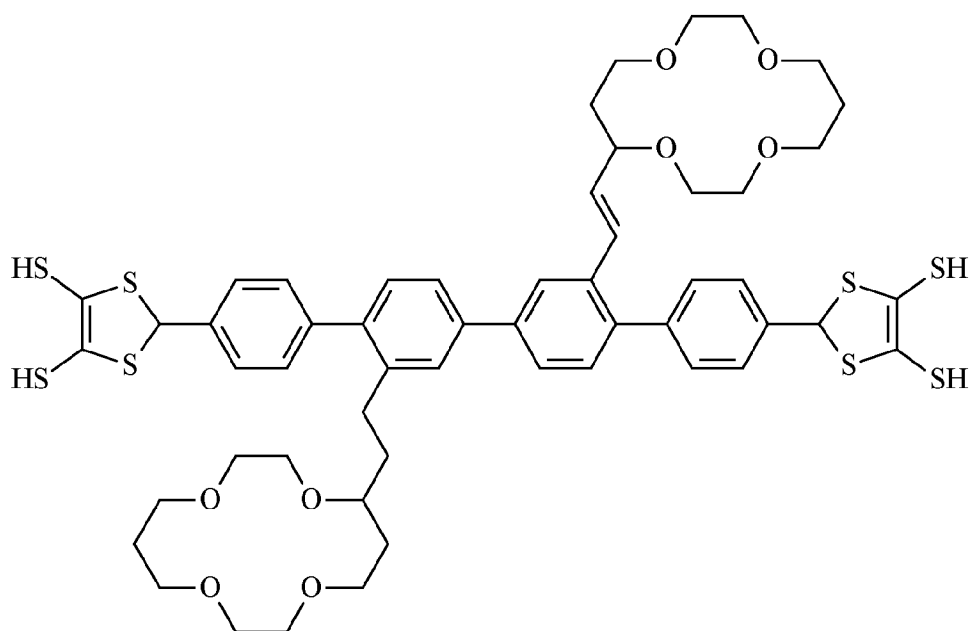
Examples of substituted oligomeric connector molecules include:

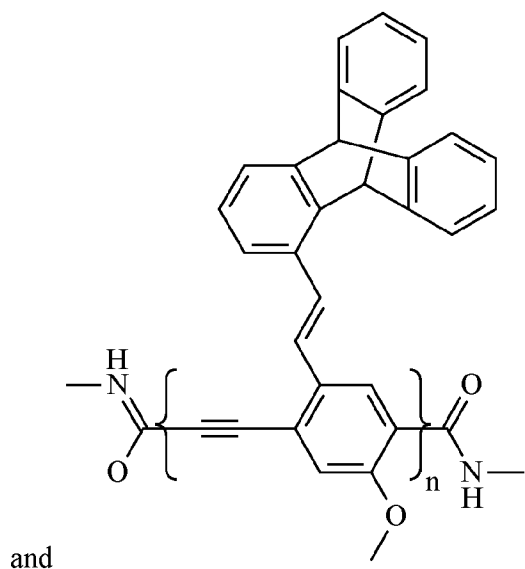






Examples of connector molecules comprising pendant groups include:





the first of which comprises crown ether pendant groups, and the second of which comprises an iptycene pendant group.

Thus, examples of conjugated polymer connector molecules include N,N'-diethyl poly(2,5-diethylaniline), bis(5-(methylthio)pyridin-3-yl)poly(ethyne), poly(5,5'-(thieno[3,2-b]thiophene-3,6-diylbis(methylene))bis(2-methylphenol)), and poly(2-(2-(3-ethyl-1H-1,2,4-triazol-1-yl)ethyl)-[1,1'-biphenyl])dithiol.

Examples of substituted oligomeric connector molecules include: 2,7-di(thiophen-2-yl)benzo[2,1-b:3,4-b']dithiophene-4,5-dione, 1,1',1'',1'''-([4,4'-bi(cyclopenta[2,1-b:3,4-b']dithiophenylidene))-2,2',6,6'-tetrayl)tetrakis(ethan-1-one), 1,2-bis(3-methoxy-2',4',6'-tris(methylthio)-[1,1'-biphenyl]-4-yl)ethyne, N,N'-([2,2':5',2'':5'',2''':5''',2''':5''',2''''-sexithiophene]-3'',4''-diylbis(methylene))bis(N-methyl-2-oxopropanamide), and 4,4',4''-(benzene-1,3,5-triyltris((3-(methylthio)phenyl)azanediyl))triphenol.

Examples of connector molecules comprising pendant groups include: 2,2'-([1,1':4',1'':4'',1''':4''',1''':4''''-quaterphenyl]-4,4''-diyl)bis(1,3-dithiole-4,5-dithiol) substituted with two or more crown ether groups and polyparaphenylene vinylene polymers substituted with iptycene groups.

The sensor component of the present invention could be designed to detect essentially any analyte, although the detection of molecular analytes in the gas or vapour phase would most likely be the area of greatest utility of the present invention.

Typically the analyte is a molecule in the gas phase or the vapour phase. The molecule may be organic or inorganic. The molecular weight of the analyte may have any value, but can be less than 1000 gmol^{-1} . In one embodiment, the analyte is an organic molecule with a molecular weight of less than 800 gmol^{-1} . The analyte can be a pharmaceutical compound.

The analyte can be a simple gaseous molecule. Detection of such compounds can be useful in an industrial environment. In one embodiment, the analyte is selected from NO , N_2O , NO_2 , N_2O_4 , SO_2 , O_2 , O_3 , CO , CO_2 , C_2H_4 , C_2H_2 , H_2 , N_2H_4 , NH_3 , H_2S , HCl , I_2 , Br_2 , Cl_2 and F_2 . The analyte can be a simple organic molecule such as an alcohol, an aldehyde, a ketone, an ester or an amine. Examples of these include methanol, ethanol, propanol and isopropanol; formaldehyde, ethanal and propanal; acetone and butanone; ethyl acetate and ethyl formate; or methyl amine, ethyl amine and amino acids. The analyte may also be selected from compounds including an aromatic group (e.g. benzene, phenol, benzylchloride, aniline or naphthalene) or a heterocyclic aromatic group (e.g. pyridine, pyrrole or quinoline or sulphur or oxygen containing heteroaromatic rings) The analyte may be any redox active gas species.

Sensors for explosives have wide ranging applications for safety and security. The analyte for the sensor component of the invention can be an explosive. In one embodiment, the analyte is an explosive compound. Examples of explosive compounds include nitro based explosive compounds. In one embodiment the explosive compound is selected from trinitrotoluene (TNT), dinitrophenol (DNP), trinitrobenzene (TNB), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), N,N'-bis-(1H-tetrazol-5-yl)-hydrazine (HBT), 2,2-Dinitroethene-1,1-diamine (DADNE), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), 2,6-dioxo-1,3,4,5,7,8-hexanitrodecahydro-1H,5H-diimidazo[4,5-b:4',5'-e]pyrazine (HHTDD) and hexamethylene triperoxide diamine (HMTD).

The sensor component may alternatively be used to detect ions and accordingly the analyte may be any ionic species including metal cations, oxo anions or conjugate bases of mineral acids. For example, the analyte may be selected from Cu^{2+} , Ca^{2+} , Hg^{2+} , Zn^{2+} , Mg^{2+} , Pb^{2+} , Cd^{2+} , and K^+ ; or the analyte may be selected from I^- , Br^- , Cl^- , F^- , SO_4^{2-} , NO_2^- , and $\text{Cr}_2\text{O}_7^{2-}$.

The sensor components of the invention can be sensitive to one or more analytes. For example, two or more different types of connector molecules could be used, or two or more groups sensitive to different analytes could be comprised in a single connector molecule.

Preferably, the interaction between the analyte and the connector molecule is reversible.

The present invention also provides a process for producing a sensor component. The process of the invention can be used to produce the sensor component of the invention
5 defined herein.

Accordingly, the invention provides a process for producing a sensor component for detecting an analyte, which process comprises:

- (a) providing an insulating substrate having a plurality of conductive nodes disposed on a surface thereof, which insulating substrate is disposed between a first electrode
10 and a second electrode;
- (b) disposing connector molecules on the substrate and thereby forming electrical junctions between separate conductive nodes or between an electrode and a conductive node, and monitoring an electrical property between the first electrode and the second electrode, which connector molecules comprise two or more groups capable of forming a
15 chemical bond with a conductive node or an electrode, and wherein the connector molecules are capable of displaying a change in an electrical property in response to interaction with an analyte; and
- (c) ceasing to dispose the connector molecules when the change in the electrical property indicates that an electrical percolation network has formed.

20 In step (b), the electrical property between the first electrode and the second electrode may be monitored by taking a plurality of discrete measurements of the electrical property, or by measuring the electrical property continuously. For instance, a first discrete measurement of the conductance or resistance may be taken before starting to dispose the connector molecules onto the substrate, and one or more further discrete measurements may be taken
25 during the step of disposing the connector molecules onto the substrate, and/or after disposing a desired amount of the connector molecules onto the substrate. Usually, however, the electrical property is measured continuously during at least part of, and more typically during the whole of, the step of disposing connector molecules onto the substrate.

In this process, any of the components (e.g. connector molecules, conductive nodes,
30 electrical property or insulating substrate) may be as defined above.

Typically, step (b) comprises:

disposing connector molecules on the substrate and thereby forming electrical junctions between separate conductive nodes or between an electrode and a conductive node, while measuring the resistance, impedance or capacitance between the first electrode and the second electrode,

5 which connector molecules comprise two or more groups capable of forming a chemical bond with a conductive node or an electrode, and wherein the connector molecules are capable of displaying a change in an electrical property in response to interaction with an analyte.

10 Usually, step (c) comprises ceasing to dispose the connector molecules when a change in the electrical property indicates that the electrical percolation network is formed in the percolation region. The percolation region is defined and discussed above.

15 The percolation region is the region in which an electrical property of the network varies most rapidly. The skilled person would be aware from measuring the variation of the electrical property as more connector molecules are disposed when the network was in the percolation region. The percolation region may also be reached by controlling the thickness of the layer of connector molecules disposed. The thickness of the layer of connector molecules may be any of those values or ranges defined above. In particular it may be, from 0.5 nm to 40 nm, or from 1 nm to 10 nm, or (as a value relative to the height of the conductive nodes) from 1% to 100% of the height of the conductive nodes.

20 Often, ceasing to dispose the connector molecules will occur when the electrical property being measured varies most rapidly as a function of the areal density of the connector molecules. For example, the disposition of the connector molecules could be stopped when the rate of change of the electrical property with respect to the change in the number of connector molecules is no longer increasing. The percolation region is the region (as the areal density of connector molecules varies) which contains this mid point and extends to the percolation threshold at the lower end and the thin film limit at the upper end. Often in practice, an experiment is performed that relates the amount of connector molecules that are deposited to the desired electrical property (e.g. resistance, capacitance, impedance, etc.) of the network. A graph is plotted to show this relationship, which will look something like
25 Figure 2. At one point within the percolation region of this graph the electrical property changes most rapidly as a function of amount of connector molecules that have been deposited. In some cases, this may be the optimal point to run the sensor. Subsequent
30

sensors may then be created that have a similar node distribution and the optimal amount of connector molecules is deposited on them.

Step (a) of the process may further comprise producing the conductive nodes on the surface of the insulating substrate, by:

- 5 (a1) providing an insulating substrate disposed between a first electrode and a second electrode;
- (a2) disposing a layer of a conductive node material on a surface of the insulating substrate wherein the conductive node material wets the surface and connects the electrodes; and
- 10 (a3) dewetting the layer of conductive node material to form isolated nodes of the conductive node material on the insulating substrate wherein the conductive node material no longer connects the electrodes.

Typically, step (a) of the process further comprises producing the conductive nodes on the surface of the insulating substrate, by:

- 15 (a1) providing an insulating substrate disposed between a first electrode and a second electrode;
- (a2) disposing a layer of a conductive node material on a surface of the insulating substrate wherein the conductive node material wets the surface and connects the electrodes;
- (a3) dewetting the layer of conductive node material and monitoring the
- 20 conductance or resistance between the first electrode and the second electrode; and
- (a4) ceasing to de-wet when the change in the conductance or resistance indicates that isolated nodes of the conductive node material have been formed.

Step (a3) typically comprises dewetting the layer of conductive node material while measuring the conductance or resistance between the first electrode and the second electrode

25 by any means, for example an ohmmeter.

If the conductance between the electrodes is being monitored, step (a4) may comprise ceasing to de-wet the conductive node material when the conductance between the first electrode and the second electrode has decreased to between $10^{12}G$ and G , between 10^9G and G , or between 10^6G and G , where G is the conductance of the insulating substrate; or,

30 if the resistance between the electrodes is being monitored, step (a4) may comprise comprises ceasing to de-wet the conductive node material when the resistance between the

first electrode and the second electrode has increased to between $10^{-12}R$ and R , between $10^{-9}R$ and R , or between $10^{-6}R$ and R , where R is the resistance of the insulating substrate.

Preferably, however, step (a4) comprises ceasing to de-wet the conductive node material when the resistance between the first electrode and the second electrode has increased to above 100 k Ω , above 50 k Ω , above 30 k Ω or above 20 k Ω , and preferably above 30 k Ω . Typically, for instance, when the conductive node material comprises gold, silver, platinum, palladium, iridium or copper (and particularly for instance when the conductive node material comprises gold), step (a4) comprises ceasing to de-wet the conductive node material when the resistance between the first electrode and the second electrode has increased to above 30 k Ω .

The increase in resistance indicates that the layer of conductive node material has dewetted to an extent that isolated nodes of the conductive material have been formed. In some cases, there may still be a continuous mass of the conductive material between two electrodes, but this will not prevent the substrate comprising the nodes from being useful in a sensor component, as the sensor component will just have a higher base conductivity than one comprising a substrate wherein there is no continuous mass of conductive node material between the two electrodes. In both cases, any connector molecules disposed will still respond to analyte molecules and cause measurable changes in an electrical property of the network.

Therefore, by combination of the above described processes, the invention also provides a process for producing a sensor component for detecting an analyte, the process comprising the steps of:

(a1) providing an insulating substrate disposed between a first electrode and a second electrode;

(a2) disposing a layer of a conductive material on a surface of the insulating substrate wherein the conductive material wets the surface and connects the electrodes;

(a3) dewetting the layer of conductive node material and monitoring the conductance or resistance between the first electrode and the second electrode;

(a4) ceasing to de-wet when the change in the conductance or resistance indicates that isolated nodes of the conductive node material have been formed;

(b) disposing connector molecules on the substrate and thereby forming electrical junctions between separate conductive nodes or between an electrode and a conductive node, and monitoring an electrical property between the first electrode and the second electrode,

which connector molecules comprise two or more groups capable of forming a chemical bond with a conductive node or an electrode, and wherein the connector molecules are capable of displaying a change in an electrical property in response to interaction with an analyte; and

(c) ceasing to dispose the connector molecules when the change in the electrical property between the first electrode and the second electrode indicates that an electrical percolation network has formed.

The process of the invention can be performed under vacuum, ultra high vacuum (UHV), an inert atmosphere or under normal atmospheric conditions.

This process allows a sensor component comprising a conductive node/connector molecule electrical percolation network to be formed. Typically, in the process of the invention the conductance (or resistance) of the component is monitored in order to establish, first, for how long the layer of conductive node material should be dewetted and, second, how many connector molecules should be disposed onto the surface of the substrate and onto the conductive nodes.

The disposition of a layer of a conductive material onto a surface of the insulating substrate can be performed by any suitable method. The conductive material for forming the conductive nodes may be disposed by vapour deposition, solution deposition or lithography. Vapour deposition comprises the following evaporation methods: thermal deposition, sputter deposition, pulsed laser deposition, molecular beam deposition, atomic layer deposition, cathodic arc deposition, electrospray deposition, and vapour deposition polymerisation. Solution deposition comprises: drop coating, spin coating, dip coating, Langmuir-Blodgett film creation, and electrochemical deposition. These techniques of deposition are known to the skilled person and the skilled person would be in a position to operate them.

The initial deposition of the conductive node material onto the insulating substrate forms a layer of the conductive node material which will connect the first electrode and the second electrode. The sensor will accordingly show a lower resistance after the formation of the layer of conductive node material between the electrodes.

Next, the conductive nodes are formed by dewetting the surface. The term “dewetting”, as used herein, refers to the process whereby a layer of a material on a surface is disrupted and the material aggregates into isolated areas (droplets). In the case of a conductive material such as a metal on the surface of a substrate this process may occur by a solid layer of the material first melting, then separating into droplets in the surface of the substrate. The process may also occur by solid state diffusion. Dewetting occurs as it minimises the surface energy of the conductive material/substrate interface, the conductive material/air (or vacuum) interface and the substrate/air (or vacuum) interface. The extent to which a material de-wets a surface depends on the surface energies of each component of the system and other factors such as temperature. Measuring the resistance of the component during dewetting allows the dewetting to be enacted for an appropriate period of time. The dewetting is stopped when the change in conductance indicates that isolated conductive nodes have been formed.

The dewetting may be stopped when the conductance of the component drops to between $10^{12}G$ and G , between 10^9G and G , or between 10^6G and G , where G is the conductance of the insulating substrate. If the resistance is measured, the following could apply. The dewetting is stopped when the resistance of the component increases to between $10^{12}R$ and R , between 10^9R and R , or between 10^6R and R , where R is the resistance of the insulating substrate.

The units Siemens (S) and ohm (Ω) are the SI derived units for conductance (G) and resistance (R) respectively. Conductivity (σ) and resistivity (ρ) are measured in $S\text{m}^{-1}$ and Ωm respectively.

Preferably, dewetting can be stopped when the resistance between the first electrode and the second electrode has increased to above $100\text{ k}\Omega$, above $50\text{ k}\Omega$, above $30\text{ k}\Omega$ or above $20\text{ k}\Omega$, and preferably to above $30\text{ k}\Omega$. Typically, for instance, when the conductive node material comprises gold, silver, platinum, palladium, iridium or copper (and particularly for instance when the conductive node material comprises gold), step (a4) comprises ceasing to de-wet the conductive node material when the resistance between the first electrode and the second electrode has increased to above $30\text{ k}\Omega$.

The length of time for which the surface is dewetted will affect the size, shape and distribution of the conductive nodes. Dewetting for a longer time will produce larger nodes separated by greater distances. If the surface is dewetted for too long then large nodes

separated by distances which are too large can be formed. The skilled person would be aware how long the surface needs to be dewetted for in order for suitable conductive nodes to be formed. The distances between the conductive nodes can be tuned to be suitable for the connector molecules. Longer connector molecules such as conjugated polymers can be
5 suited to further separated nodes, although longer molecules can also be suited to closely spaced nodes as nodes will often be large relative to the length of the connector molecule and connector molecules longer than the distance between two nodes can connect these two nodes via the centre of each node or even via the two opposite sides of each node. Shorter connector molecules such as monomeric species will require smaller gaps between nodes.
10 The morphology of the conductive nodes disposed on the insulating substrate can be investigated using SEM or AFM. Once the morphology of the surface has been investigated, the time and conditions used for dewetting can be altered accordingly.

The height (maximum thickness) of a conductive node may be defined as the distance between the surface of the insulating substrate on which the node is disposed and the upper
15 surface of the node. Usually, the height of the conductive nodes disposed on the surface of the insulating substrate, is equal to or less than 500 nm. Typically, the average thickness of the conductive nodes is from 0.3 nm to 200 nm. The average thickness may for instance be from 5 nm to 100 nm, or preferably from 20 nm to 40 nm.

Typically, the size of a conductive node that is disposed on the surface of the
20 insulating substrate, is from 1 nm to 5000 nm, or from 1 nm to 2000 nm. Usually, size is from 10 nm to 500 nm, or from 15 nm to 150 nm. The size of a node is, if the node is circular, the diameter of the node (measured parallel to the surface of the substrate), or, if the node is not circular, the diameter of a circular node occupying the same area on the substrate (measured parallel to the surface of the substrate).

25 The distance between any two adjacent nodes is typically from 0.1 nm to 100 nm or from 0.5 nm to 50 nm. Usually, the distance between two adjacent nodes is from 5 nm to 10 nm.

The height, diameter and distance between the nodes can all be measure by scanning electron microscopy (SEM) or atomic force microscopy (AFM).

30 Dewetting of the conductive node material layer in order to produce such nodes can be performed by any suitable technique. Suitable techniques include those which allow

significant amounts of solid state diffusion to occur or those which melt the layer of conductive node material and allow the conductive material to form into droplets. In one embodiment, dewetting is performed by heating the insulating substrate. If the dewetting is performed by heating, the component or substrate can be heated to about 50°C, about 100°C, 5 about 150°C, about 200°C, about 300°C, about 400°C, about 500°C, about 600°C, about 700°C, about 800°C, about 900°C, about 1000°C, about 1100°C, or about 1200°C. The dewetting can be performed under UHV conditions or under other conditions. Dewetting can be performed for any suitable period of time depending on the thickness of the starting layer of conductive node material. Dewetting can be performed for 1 second to 200 hours, 2 10 seconds to 160 hours, 1 minute to 40 hours or any length of time in between any of these values.

Any dewetting step or dewetting process used in the invention may also include an additional process selected from electron beam exposure, ion beam exposure, and laser induced dewetting can aid dewetting. There are also other ways for controlled dewetting, 15 such as using patterned substrate for templated dewetting, or antimony sacrificial layer assisted dewetting to create a desired node network.

Steps (a1) to (a3) or steps (a1) to (a4) of the above described process produce an insulating substrate between two electrodes on which conductive nodes are disposed. The conductive node/connector molecule electrical percolation network is then formed by the 20 deposition of connector molecules onto the insulating substrate between two electrodes on which conductive nodes are disposed (steps (b) and (c) of the process).

The connector molecules can be disposed in any suitable way. Often this will involve forming a vapour of the connector molecules which can then condense onto the component surface. The connector molecules can also be deposited by applying a solution of connector 25 molecules to the surface and then allowing the solvent in the solution to evaporate leaving deposited mass of connector molecules. In one embodiment, the connector molecules may be disposed by vapour deposition, solution deposition or lithography. Vapour deposition comprises the following evaporation methods: thermal deposition, sputter deposition, pulsed laser deposition, molecular beam deposition, atomic layer deposition, cathodic arc deposition, 30 electrospray deposition, and vapour deposition polymerisation. Solution deposition comprises: drop coating, spin coating, dip coating, Langmuir-Blodgett film creation, and electrochemical deposition.

The time for which the connector molecules are to be deposited on the surface of the component (comprising the insulating substrate and the conductive nodes) is determined by measuring an electrical property between the electrodes as the connector molecules are deposited onto the surface by any of the above mentioned techniques. While the connector molecules are deposited and form connections between the nodes, the electrical property will change. Monitoring this change allows the deposition to be stopped when a number of molecules suitable to form a percolation network has been deposited. This is as described above.

In one embodiment, the disposition of the connector molecules is stopped when the change in the electrical property indicates that an electrical percolation network has formed. In a preferred embodiment, the disposition of the connector molecules is stopped when the change in the conductance or the resistance indicates that the electrical percolation network is formed in the percolation region with respect to an electrical property.

If the resistance between the electrodes is being measured, the disposing of the connector molecules may for instance be stopped when the resistance between the first and the second electrodes has decreased by at least 5 k Ω . Thus, the disposing of the connector molecules may for example be stopped when the resistance between the first and the second electrodes has decreased by at least 5 k Ω , and at most to the resistance of a thin film of the connector molecules. Ceasing disposition of the connector molecules may also occur at any of the points as described above (e.g. when the electrical property varies most rapidly as a function of the areal density of connector molecules).

The disposition of the connector molecules may also be stopped when the thickness of the layer of connector molecules deposited is as defined above, i.e. from 0.5 nm to 40 nm, from 1 nm to 10 nm, or from 1% to 100% of the height of the conductive nodes.

The electrodes used in the process provided by the invention are typically the same as those described above for the sensor component of the invention, and may therefore be as further defined hereinbefore for the sensor component of the invention.

Likewise, the insulating substrates used in the process provided by the present invention may be the same as those described above for the sensor component of the invention, and may therefore be as further defined hereinbefore for the sensor component of the invention.

The conductive material disposed on the surface of the insulating substrate in the process of the present invention can comprise any suitable conductive material capable of forming an array of conductive nodes when dewetted. In one embodiment, the conductive material comprises a metal selected from groups 3 to 16 of the periodic table of the elements, a conducting oxide, a conducting organic material or a mixture thereof. In one embodiment, the conductive material comprises gold, silver, platinum, palladium, iridium, copper, tungsten (IV) oxide, iron (II, III) oxide or a mixture thereof. In a preferred embodiment, the conductive node material comprises gold.

Examples of metals selected from groups 3 to 16 of the periodic table of the elements include scandium, yttrium, lanthanum, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, copper, silver, gold, zinc, cadmium, mercury, aluminium, indium, tin, lead, antimony and bismuth. The conductive node material can comprise any of these materials.

In one embodiment, the conductive node material comprises a material which is capable of dewetting the insulator surface. A material will dewet on a surface if this decreases the total surface energy of the system. In order for the conductive node material to dewet the insulating substrate the surface energy of the insulating substrate must be less than the sum of the surface energy of the conductive node material and the interface energy of the insulating substrate and the conductive node material. Accordingly, in one embodiment,

$$\gamma_{IS} < \gamma_{CNM} + \gamma_{IS:CNM}$$

wherein γ_{IS} is the surface energy of the insulating substrate, γ_{CNM} is the surface energy of the conductive node material and $\gamma_{IS:CNM}$ is the interface energy between the insulating substrate and the conductive node material. This will be true for a wide range of conductive node materials and insulating substrates. The skilled person will be aware which conductive materials would be appropriate.

The connector molecules used in the process of the present invention are typically the same as those described above for the sensor component of the present invention, and may therefore be as further defined hereinbefore for the sensor component of the invention.

The sensor component produced by the process of the present invention could be designed to detect essentially any analyte, as described hereinbefore in relation to the sensor component of the invention.

5 The present invention also provides a sensor component which is obtainable by the process of the invention as defined herein for producing a sensor component.

The present invention also provides a device comprising a sensor component according to the invention or a sensor component obtainable by the process of the invention.

10 Sensor components for analytes can be used in a wide range of devices. The device may be a sensor, an alarm, a warning system, a detector, a spectrometer, a kit, a transistor or a diode.

Typically the device is a sensor. Accordingly, the present invention also provides a sensor comprising: a sensor component according to the invention or a sensor component which is obtainable by the process of the invention.

15 The device or sensor usually further comprises a detection means operably connected to the first and second electrodes of the sensor component. The detection means is typically capable of detecting a change in an electrical property of the sensor component due to the interaction of an analyte with the connector molecules. Usually, the detection means is capable of detecting a change in the electrical resistance, conductance or capacitance of the sensor component. The detection means may for instance be an ohmmeter.

20 The invention also provides the use of a device of the invention for detecting an analyte.

In particular, the invention provides the use of a sensor of the invention for detecting an analyte.

25 The device or sensor of the present invention could be designed to detect essentially any analyte. The analyte may be any analyte as defined above.

The invention further provides a process for producing a plurality of conductive nodes on a surface of an insulating substrate, which process comprises:

(a) providing an insulating substrate disposed between a first electrode and a second electrode;

(b) disposing a layer of a conductive node material on a surface of the insulating substrate wherein the conductive node material wets the surface and connects the electrodes; and

5 (c) dewetting the layer of conductive node material to form isolated nodes of the conductive node material on the insulating substrate.

Any of the components (e.g. insulating substrate, electrode or conductive node material) or process steps (e.g. disposing the conductive node material or dewetting) in this process may be as defined anywhere above.

10 The process may be as further defined hereinbefore for steps (a1) to (a3) of the process of the invention for producing a sensor component.

Thus, usually, step (c) comprises:

(c1) dewetting the layer of conductive node material and monitoring the conductance or resistance between the first electrode and the second electrode; and

15 (c2) ceasing to de-wet when the change in the conductance or resistance indicates that isolated nodes of the conductive node material have been formed.

Preferably, Step (c2) may for instance comprise ceasing to de-wet the conductive node material when the resistance between the first electrode and the second electrode has increased to above 100 k Ω , above 50 k Ω , above 30 k Ω or above 20 k Ω , and preferably above 30 k Ω . Typically, for instance, when the conductive node material comprises gold, silver, 20 platinum, palladium, iridium or copper (and particularly for instance when the conductive node material comprises gold), step (c2) comprises ceasing to de-wet the conductive node material when the resistance between the first electrode and the second electrode has increased to above 30 k Ω .

25 The process may further comprise removing the first electrode and the second electrode from the insulating substrate.

The terms “a”, “an” and “the”, as used herein, indicate the single or the plural. Terms in the singular include the plural and vice versa. The terms “one or more” and “two or more” refer to 1, 2, 3, 4, 5, 6 or more and 2, 3, 4, 5, 6 or more respectively. The term “at least some” as used herein indicates more than 0.01%, more than 0.1% or more than 1% of the 30 available matter.

The invention will now be further described in the following examples.

EXAMPLE

Example 1 – Sensor component construction 1

A sensor component according to the invention comprising an Au/ α -sexithiophene electrical percolation network was produced by the following method.

A magnesium oxide (001) single crystal [manufactured by SurfaceNet GmbH, supplied by PI-KEM Ltd, UK.] was provided as the insulating substrate between two platinum electrodes. The electrodes were 1 mm apart and were deposited through sputter coating. A 4.5 to 5.0 nm thick layer of Au was deposited onto this substrate between the electrodes by thermal evaporation. The Au [supplied by Goodfellow, 99.95% purity] evaporation was performed by heating a tungsten boat [supplied by Leybold Optics] containing Au in a high vacuum system [$\sim 10^{-5}$ Pa pressure] and evaporating it at a rate of 0.1 nm/second. Once the layer of Au had been deposited the surface morphology of the Au layer was examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The resulting SEM image is shown in Figure 3 and confirms that a layer of Au was formed.

The network of gold nodes was then created through a dewetting process. The MgO (001) single crystal substrate and Au layer were annealed at 200°C under ultra-high vacuum (UHV) [$\sim 10^{-8}$ Pa chamber base pressure] until the resistance of the component increased above 30 k Ω indicating that the Au layer had dewetted the surface to form a network of nodes. The resulting Au on MgO (001) network had a resistance of ~ 30 k Ω in the UHV chamber, and this resistance increased to ~ 148 k Ω when the sample was removed from the UHV chamber. The surface was examined again with SEM and AFM to confirm that a suitable network of conductive Au nodes had been formed. Figure 4 shows the resulting image, which demonstrates that this was indeed the case.

The sample was then transferred to another high vacuum system (base pressure $\sim 10^{-3}$ Pa) equipped with a gas handling facilities. The sample electrodes were connected to a Keithley 2400 multimeter and the resistance of the network was monitored and recorded in real time using LabVIEW software.

As a control, the response of the Au network to the presence of air was tested. The MgO/Au sample was exposed to air for brief periods of time and the change in resistance of

the sample was measured. The results for this are shown in the portion of Figure 5 corresponding to 0 to 500 seconds. An increase in resistance of around 300 Ω is observed on exposure of the Au only network to air.

In the same chamber α -sexithiophene was then deposited onto the sample by thermal evaporation from a tungsten boat at a rate of 0.2nm/second. The layer thickness of the oligomer was monitored in situ via a quartz crystal microbalance (Q-Pod, Inficon) placed at the same distance from the source as the sample. A layer of 10nm thickness of α -sexithiophene was deposited. The deposition of the α -sexithiophene on the surface caused a rapid decrease in resistance of the sample. α -sexithiophene deposition was stopped when the resistance of the sample had dropped to 141.5 k Ω . This deposition lead to the formation of a Au/sexithiophene electrical percolation network. The response of this mixed network to the presence of air was measured. As can be seen from Figure 5, the change in resistance of the mixed Au/sexithiophene was twice that of the Au only network.

The response of the sample to two other analytes was investigated. In Figure 6 the change in resistance of the sample upon exposure to moisture and alcohol is shown. Changes of several k Ω are observed in both cases and the high sensitivity of the Au/ α -sexithiophene percolation network is clear.

Example 2 – *Dewetting process*

A film of 4.7 nm of Au was evaporated onto an MgO (001) single crystal decorated with two Pt electrodes separated by 1mm. This sample was then transferred into an ultra high vacuum chamber. The resistance between two Pt electrodes was measured. The sample was annealed in ultra high vacuum at increasing temperatures starting at 3850 seconds and finishing at 200 °C at 7990 seconds. From 3850 seconds to 7990 seconds the temperature was increased by 15 °C every 5 minutes.

The resistance plotted as a function of time is shown Figure 7. In the figure three main regions can be seen: the smoothing region, where the disordered evaporated Au film starts to order resulting in a slight lowering of the resistance; the dewetting region, where there is a substantial increase of the resistance as the nodes start to form exposing insulting regions between them; and the ripening region, where the number of nodes decreases and the size of the nodes and their average separation increases. Typically, annealing is stopped after the

dewetting stage is completed i.e. around 12000 seconds in Figure 7. However, it is possible to fine-tune the node separation by continuing the anneal for a longer time past that stage.

Example 3 – *Sensor component construction 2*

5 A 5 nm layer of gold deposited on an MgO (001) single crystal substrate was annealed at 700°C. Figures 8 and 9 show SEM images of the samples before and after annealing at 700°C. This demonstrates the process of dewetting.

The sample conductivity was measured during the annealing phase. A similar curve as that shown in Figure 7 for Example 2 was observed indicating that the Au film undergoes three processes: (1) smoothing, where roughness following the deposition is annealed out and results in a lowering of the conductivity; (2) dewetting, where the continuous film starts to break up into individual particles and exposes the insulating MgO substrate, resulting in an increase of the resistance; (3) ripening, where the individual particles increase in size and more substrate is exposed resulting in a further increase in resistance.

15 Sexithiophene was deposited on the gold scaffold produced by the annealing process while resistance of the sample was continuously measured. Figure 10 shows the change of resistance with increased deposition amount of sexithiophene onto the Au nanoparticle scaffold. At the initial deposition stage, the sample resistance decreases dramatically for sexithiophene coverage of less than approximately 7 nm thickness. This demonstrates that the Au-sexithiophene network is in the percolation threshold regime. The curve then levels off indicating the thin film regime.

Figure 11 shows the first derivative of a curve fitted to the decrease of resistance with increasing sexithiophene layer thickness (as shown in Figure 10). The point where the resistance changes most dramatically as a function of sexithiophene thickness is at 3.3nm, indicating the best thickness to operate the sensor at for maximum sensitivity.

25 The sensing response of the Au-sexithiophene component was then measured for exposure to a number of analytes. Figure 12 shows the sensing response for a sensor operating in the percolation regime (3.3 nm thickness, upper curve A) versus one operating in the thin film regime (23 nm thickness, lower curve B). The testing gas was saturated H₂O vapour in a N₂ carrier gas at a total pressure of 5.5×10^{-4} torr. This figure demonstrates that the sensor is far more sensitive when operating in the percolation regime. Figure 13 shows

the change in resistance after exposure to different pressures of reactants. There is a greater response from the percolation sensor (3.3 nm thickness of sexithiophene) when the pressure of the saturated H₂O vapour in a N₂ carrier gas is increased. Curve B was taken at 4×10^{-4} torr. The pressure was then increased to 5.5×10^{-4} torr for the curve A.

- 5 The sensing response was then tested for exposure to three different gasses: nitrogen, ethanol and water. The sensor was exposed several times to each analyte. Figure 14 shows the response of the percolation sensor to these three different gasses, all at a pressure of 5.5×10^{-4} torr. The response to N₂ (A) on its own is the smallest. The response to saturation vapour pressure of ethanol in N₂ is the next greatest (B). The greatest response is for
- 10 saturated H₂O vapour in a N₂ carrier gas (C).

It has been demonstrated that sensor components can be constructed which operate in the percolation threshold regime. Such sensor components demonstrate greatly improved sensitivity.

CLAIMS

1. A sensor component for detecting an analyte comprising:

(i) a first electrode and a second electrode;

5 (ii) an insulating substrate disposed between the first electrode and the second electrode;

(iii) a plurality of conductive nodes disposed on a surface of the insulating substrate; and

10 (iv) a plurality of connector molecules comprising two or more groups capable of forming a chemical bond with a conductive node or an electrode, which connector molecules are capable of displaying a change in an electrical property in response to interaction with an analyte;

wherein at least some of the connector molecules are bonded to one or more nodes, or to one electrode, and thereby electrical junctions are formed between separate nodes or
15 between a node and an electrode;

and wherein the electrical junctions form an electrical percolation network, which electrical percolation network comprises at least one continuous pathway of connector molecules and conductive nodes which connects the first electrode and the second electrode.

20 2. A sensor component according to claim 1 wherein the number and configuration of junctions in the electrical percolation network is such that the percolation network is between the percolation threshold and the thin-film limit.

3. A sensor component according to claim 1 or claim 2 wherein the number and
25 configuration of junctions in the electrical percolation network is such that the percolation network is in the percolation region.

4. A sensor component according to any one of claims 1 to 3 wherein the thickness of the film of connector molecules is from 0.5 nm to 40 nm.

30

5. A sensor component according to any one of claims 1 to 4 wherein the thickness of the film of connector molecules is from 1% to 100% of the height of the conductive nodes.

6. A sensor component according to any one of the preceding claims wherein the first electrode and the second electrode independently comprise: a metal selected from groups 3 to 16 of the periodic table of the elements, graphite, a conducting oxide, a conducting nitride, a conducting carbide or a mixture thereof.

5

7. A sensor component according to any one of the preceding claims wherein the first electrode and the second electrode independently comprise platinum, palladium, copper, gold, silver, zinc, indium tin oxide, graphite or a mixture thereof.

10 8. A sensor component according to any one of the preceding claims wherein the first electrode and the second electrode are interdigitated.

9. A sensor component according to any one of the preceding claims wherein the component comprises one or more further electrodes.

15

10. A sensor component according to claim 9 wherein one or more of the further electrodes is a back-gate.

11. A sensor component according to any one of the preceding claims wherein the insulating substrate comprises magnesium oxide, strontium titanate, beryllium oxide, aluminium oxide, aluminium nitride, silicon oxide or a mixture thereof.

20

12. A sensor component according to any one of the preceding claims wherein the insulating substrate is in the form of a single crystal.

25

13. A sensor component according to any one of the preceding claims wherein the conductive nodes comprise a metal selected from groups 3 to 16 of the periodic table of the elements, a conducting oxide, a conducting nitride, a conducting carbide, a conducting organic compound or a mixture thereof.

30

14. A sensor component according to claim 13 wherein the conductive nodes comprise gold, silver, platinum, palladium, iridium, copper, tungsten (IV) oxide, iron (II, III) oxide or a mixture thereof.

15. A sensor component according to claim 13 wherein the conductive nodes comprise gold.
16. A sensor component according to any one of the preceding claims wherein the
5 connector molecules comprise conjugated molecules.
17. A sensor component according to claim 16 wherein the connector molecules comprise conjugated oligomers or polymers, or a mixture thereof.
- 10 18. A sensor component according to claim 16 or claim 17 wherein the connector molecules are selected from polyacetylenes, polyphenylenes, polyparaphenylenes, polyparaphenylene vinylenes, polyparaphenylene acetylenes, polyazulenes, polynaphthalenes, polypyrenes, polyanilines, polyparaphenylene sulphides, polyfluorenes, polypyrroles, polythiophenes, polythieno[3,2-b]thiophene, polycarbazoles, polyindoles,
15 polyazepines, or a mixture thereof.
19. A sensor component according to claim 16 or claim 17 wherein the connector molecules are selected from tetrathiafulvalene, tetraselenafulvalene, dithiophene-tetrafulvalene, tetrathiatetracene, N,N,N',N'-tetramethyl-phenylenediamine and
20 trimethoxybenzene or a mixture thereof.
20. A sensor component according to any one of the preceding claims wherein the connector molecules are selected from polythiophenes and oligomers of thiophene.
- 25 21. A sensor component according to any one of the preceding claims wherein the connector molecules comprise a pendant group, A, which is selective for an analyte.
22. A sensor component according to any one of claims 16 to 20 wherein the connector molecules are substituted with one or more groups of formula -X-A, wherein X is a bond or a
30 unsubstituted or substituted C₁₋₁₀ alkylene group and A is a pendant group selective for an analyte.

23. A sensor component according to claim 21 or claim 22 wherein A is an amine, ester, crown-ether, cryptand, C₁-C₃₀ aryl, C₁-C₃₀ heteroaryl, fullerene, iptycene, cyclodextrin, calixerene, metallocene, enzyme or antibody.

5 24. A sensor component according to any one of the preceding claims wherein the connector molecules comprise two groups capable of forming chemical bonds with a conductive node or an electrode and are linear.

10 25. A sensor component according to any one of the preceding claims wherein the groups capable of forming chemical bonds with a conductive node or an electrode are independently selected from sulfur containing groups, selenium containing groups, nitrogen containing groups, oxygen containing groups, phosphorus containing groups and carbon containing groups.

15 26. A sensor component according to any one of the preceding claims wherein the groups capable of forming chemical bonds with a conductive node or an electrode are independently selected from thiol, disulfide, thioether, thioester, sulfoxide, sulfone, thiosulfinate, sulfimine, sulfoximine, sulfonamide, sulfonediimine, thioketone, thioaldehyde, selenol, selenide, diselenide and selenoxide, amine, amide, imine, imide, nitrile, nitrate, hydroxyl, ketone,
20 aldehyde, acetal, carboxylic acid, ester, ether, phosphine, phosphate, phosphite, phosphonite, phosphinite, alkenyl and alkynyl groups.

27. A sensor component according to any one of the preceding claims wherein the groups capable of forming chemical bonds with a conductive node or an electrode are independently
25 selected from thiol, disulfide, thioether, thioester, sulfoxide, sulfone, thiosulfinate, sulfimine, sulfoximine, sulfonamide, sulfonediimine, thioketone and thioaldehyde groups.

28. A sensor component according to any one of the preceding claims wherein the each connector molecule comprises a conjugated moiety and wherein the groups capable of
30 forming chemical bonds with a conductive node or an electrode are bonded directly to the conjugated moiety.

29. A sensor component according to any one of the preceding claims wherein the bonds between the connector molecules and the nodes or electrodes are covalent or ionic.

30. A sensor component according to any one of the preceding claims wherein the electrical property of the connector molecules which changes in response to interaction with an analyte is resistance, impedance, capacitance, permeability, permittivity, magneto-resistivity or dielectric strength.

31. A sensor component according to any one of the preceding claims wherein the electrical property of the connector molecules which changes in response to interaction with an analyte is resistance, impedance or capacitance.

32. A sensor component according to any one of the preceding claims wherein the connector molecules are sexithiophene.

33. A sensor component according to any one of the preceding claims wherein the analyte is a molecule in the gas phase or the vapour phase.

34. A sensor component according to any one of the preceding claims wherein the analyte is an organic molecule with a molecular weight of less than 800 g mol⁻¹.

35. A sensor component according to any one of the preceding claims wherein the analyte is selected from NO, N₂O, NO₂, N₂O₄, SO₂, O₂, O₃, CO, CO₂, C₂H₄, C₂H₂, H₂, N₂H₄, NH₃, H₂S, HCl, I₂, Br₂, Cl₂, or F₂.

36. A sensor component according to any one of the preceding claims wherein the analyte is an explosive compound.

37. A sensor component according to claim 36 wherein the explosive is selected from trinitrotoluene (TNT), dinitrophenol (DNP), trinitrobenzene (TNB), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), *N,N'*-bis-(1*H*-tetrazol-5-yl)-hydrazine (HBT), 2,2-Dinitroethene-1,1-diamine (DADNE), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), 2,6-dioxo-1,3,4,5,7,8-hexanitrodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine (HHTDD) and hexamethylene triperoxide diamine (HMTD).

38. A process for producing a sensor component for detecting an analyte, which process comprises:

(a) providing an insulating substrate having a plurality of conductive nodes disposed on a surface thereof, which insulating substrate is disposed between a first electrode and a second electrode;

(b) disposing connector molecules on the substrate and thereby forming electrical junctions between separate conductive nodes or between an electrode and a conductive node, and monitoring an electrical property between the first electrode and the second electrode,

which connector molecules comprise two or more groups capable of forming a chemical bond with a conductive node or an electrode, and wherein the connector molecules are capable of displaying a change in an electrical property in response to interaction with an analyte; and

(c) ceasing to dispose the connector molecules when the change in the electrical property between the first electrode and the second electrode indicates that an electrical percolation network has formed.

39. A process according to claim 38 wherein step (c) comprises: ceasing to dispose the connector molecules when the change in the electrical property indicates that the electrical percolation network is formed in the percolation region.

40. A process according to claim 38 or claim 39 wherein step (c) comprises: ceasing to dispose the connector molecules when the electrical property varies most rapidly as a function of the number of connector molecules disposed.

41. A process according to any one of claims 38 to 40, wherein step (c) comprises: ceasing to dispose the connector molecules occurs when the thickness of the layer of connector molecules is from 0.5 nm to 40 nm.

42. A process according to any one of claims 38 to 41 which further comprises producing the plurality of conductive nodes on the surface of the insulating substrate, by:

(a1) providing an insulating substrate disposed between a first electrode and a second electrode;

(a2) disposing a layer of a conductive node material on a surface of the insulating substrate wherein the conductive node material wets the surface and connects the electrodes; and

(a3) dewetting the layer of conductive node material to form isolated nodes of the conductive node material on the insulating substrate.

43. A process according to any one of claims 38 to 42 which further comprises producing the plurality of conductive nodes on the surface of the insulating substrate, by:

(a1) providing an insulating substrate disposed between a first electrode and a second electrode;

(a2) disposing a layer of a conductive node material on a surface of the insulating substrate wherein the conductive node material wets the surface and connects the electrodes;

(a3) dewetting the layer of conductive node material and monitoring the conductance or resistance between the first electrode and the second electrode; and

(a4) ceasing to de-wet when the change in the conductance or resistance indicates that isolated nodes of the conductive node material have been formed.

44. A process according to claim 43 wherein step (a4) comprises ceasing to de-wet the conductive node material when the resistance between the first electrode and the second electrode has increased to above 30 k Ω .

45. A process according to any one of claims 42 to 44 wherein the conductive node material is disposed on the surface of the insulating substrate by vapour deposition, solution deposition or lithography.

46. A process according to any one of claims 42 to 45 wherein the dewetting is performed by heating the insulating substrate.

47. A process according to any one of claims 38 to 46 wherein the connector molecules are disposed onto the surface by vapour deposition, solution deposition or lithography.

48. A process according to any one of claims 38 to 47 wherein the first electrode and the second electrode are as defined in any one of claims 6 to 8.

49. A process according to any one of claims 38 to 48 wherein the insulating substrate comprises magnesium oxide, strontium titanate, beryllium oxide, aluminium oxide, aluminium nitride, silicon oxide or a mixture thereof

50. A process according to any one of claims 38 to 49 wherein the insulating substrate is in the form of a single crystal.

5 51. A process according to any one of claims 41 to 50 wherein

$$\gamma_{IS} < \gamma_{CNM} + \gamma_{IS:CNM}$$

10 and γ_{IS} is the surface energy of the insulating substrate, γ_{CNM} is the surface energy of the conductive node material and $\gamma_{IS:CNM}$ is the interface energy between the insulating substrate and the conductive node material.

52. A process according to any one of claims 41 to 51 wherein the conductive node material comprises a metal selected from groups 3 to 16 of the periodic table of the elements,
15 a conducting oxide, a conducting organic compound or a mixture thereof.

53. A process according to any one of claims 41 to 52 wherein the conductive node material comprises gold, silver, platinum, palladium, iridium, copper, tungsten (IV) oxide, iron (II, III) oxide or a mixture thereof.
20

54. A process according any one of claims 41 to 53 wherein the conductive node material comprises gold.

55. A process according to any one of claims 38 to 54 wherein the conductive nodes are
25 as defined in any one of claims 13 to 15.

56. A process according to any one of claims 34 to 55 wherein the connector molecules are as defined in any one of claims 16 to 23.

30 57. A sensor component which is obtainable by a process as defined in any one of claims 38 to 56.

58. A device comprising a sensor component as defined in any one of claims 1 to 37 and
57.

59. A device according to claim 58 wherein the device is a sensor, an alarm, a warning system, a detector, a spectrometer, a kit, a transistor or a diode.

5 60. A device according to claim 59 which is a sensor.

61. A device according to any one of claims 58 to 60 which further comprises a detection means operably connected to the first and second electrodes of the sensor component.

10 62. A device according to claim 61 wherein the detection means is capable of detecting a change in an electrical property of the sensor component due to the interaction of an analyte with the connector molecules.

15 63. A device according to claim 61 or claim 62 wherein the detection means is capable of detecting a change in the electrical resistance, impedance or capacitance of the sensor component.

20 64. A device according to claim 61 or claim 62 wherein the detection means is an ohmmeter.

65. Use of a sensor component as defined in any one of claims 1 to 37 or 57 for detecting an analyte.

25 66. Use of a device as defined in any one of claims 58 to 64 for detecting an analyte.

67. Use according to claim 65 or claim 66 wherein the analyte is as defined in any one of claims 33 to 37.

30 68. A process for producing a plurality of conductive nodes on a surface of an insulating substrate, which process comprises:

(a) providing an insulating substrate disposed between a first electrode and a second electrode;

(b) disposing a layer of a conductive node material on a surface of the insulating substrate wherein the conductive node material wets the surface and connects the electrodes; and

5 (c) dewetting the layer of conductive node material to form isolated nodes of the conductive node material on the insulating substrate.

69. A process according to claim 68 wherein step (c) comprises:

(c1) dewetting the layer of conductive node material and monitoring the conductance or resistance between the first electrode and the second electrode; and

10 (c2) ceasing to de-wet when the change in the conductance or resistance indicates that isolated nodes of the conductive node material have been formed.

70. A process according to claim 69 wherein step (c2) comprises ceasing to de-wet the conductive node material when the resistance between the first electrode and the second
15 electrode has increased to above 30 k Ω .

71. A process according to any one of claims 68 to 70 which is as further defined in any one of claims 45 to 54.

20 72. A process according to any one of claims 68 to 71 which further comprises removing the first electrode and the second electrode from the insulating substrate.

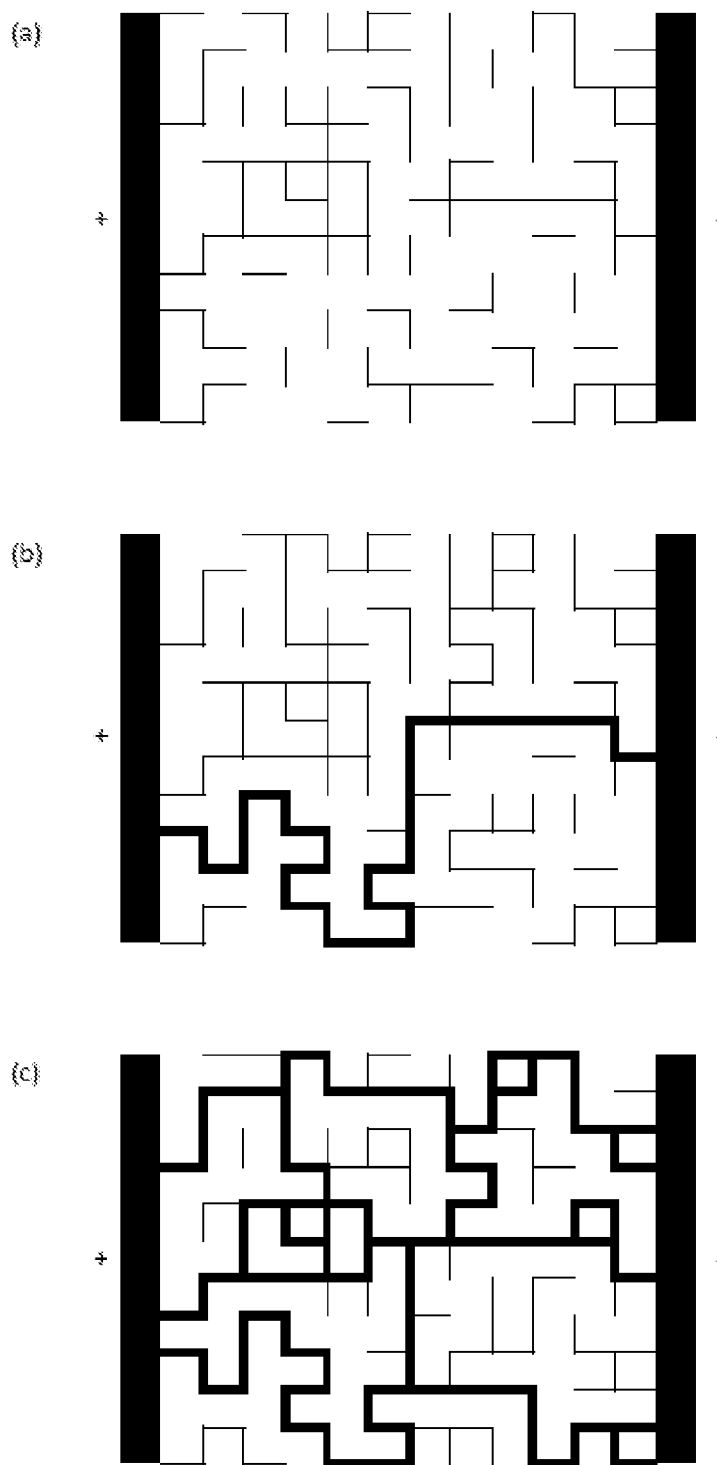
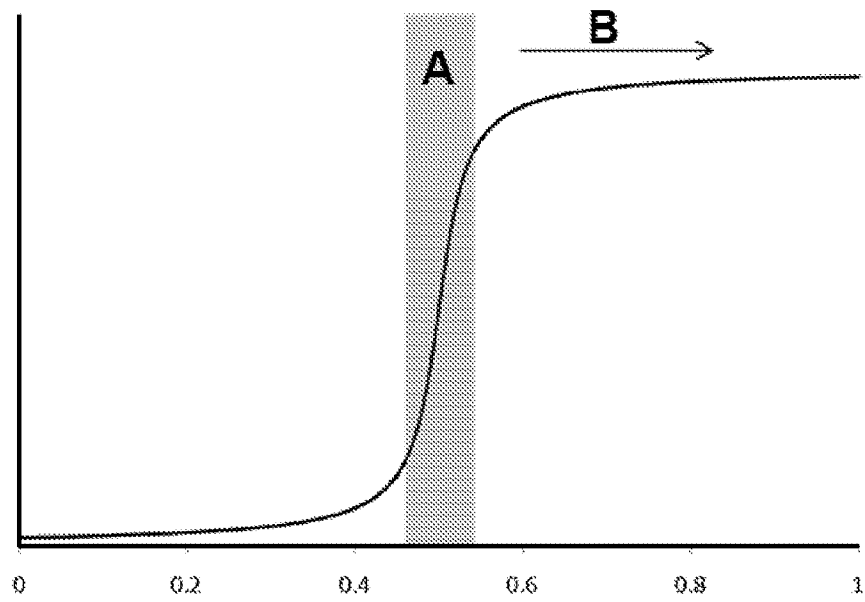
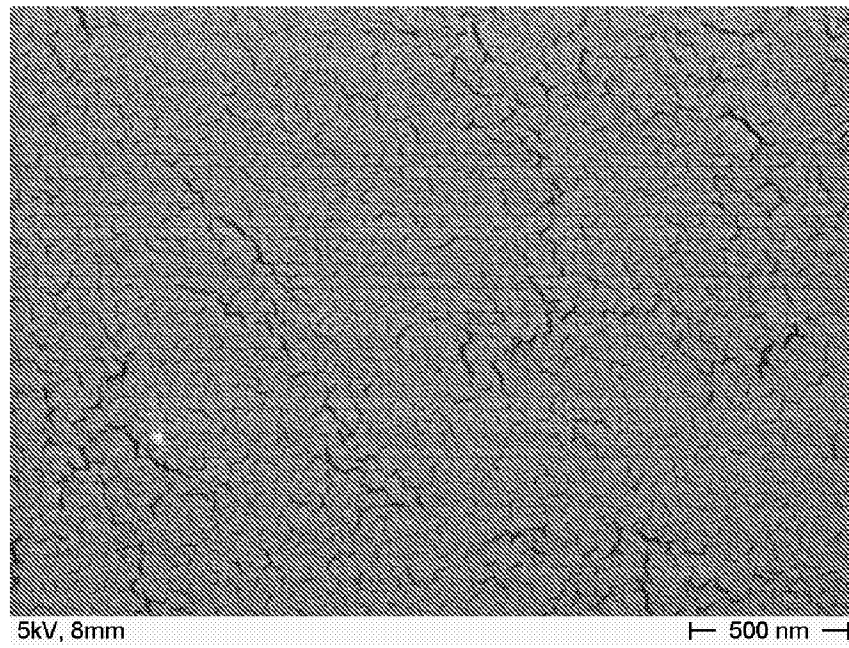


Fig. 1

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**Fig. 2****Fig. 3**

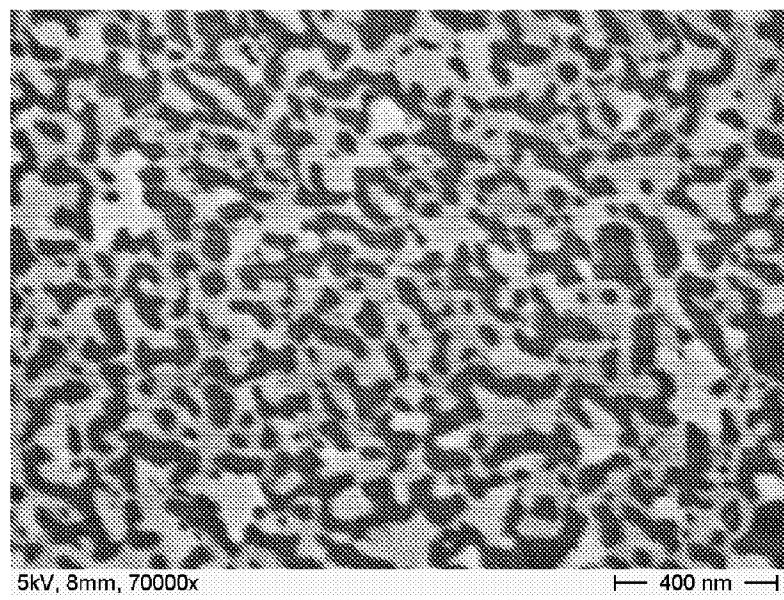


Fig. 4

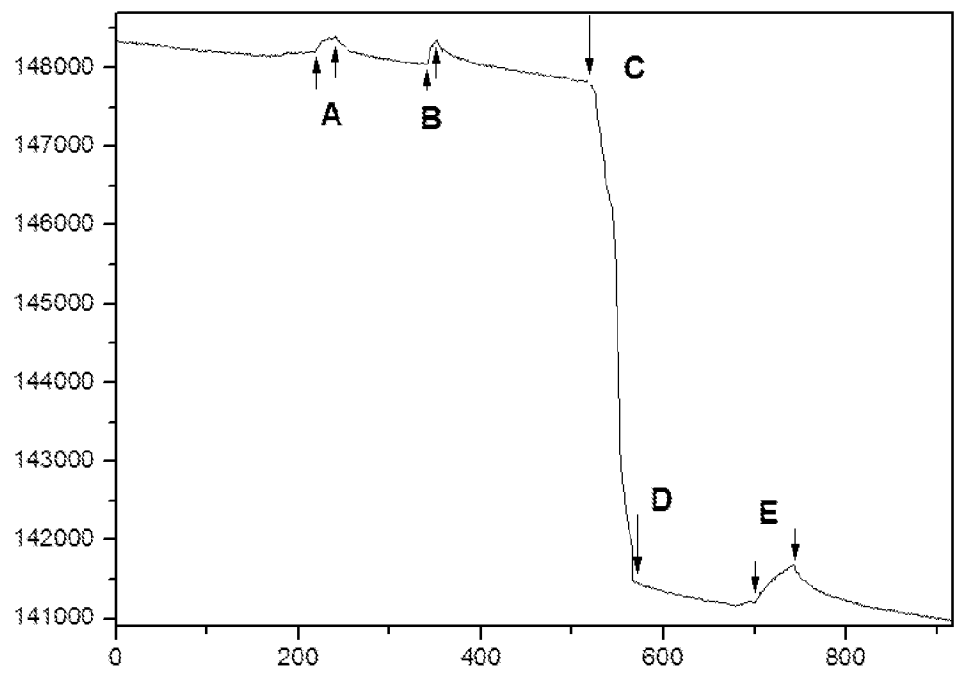


Fig. 5

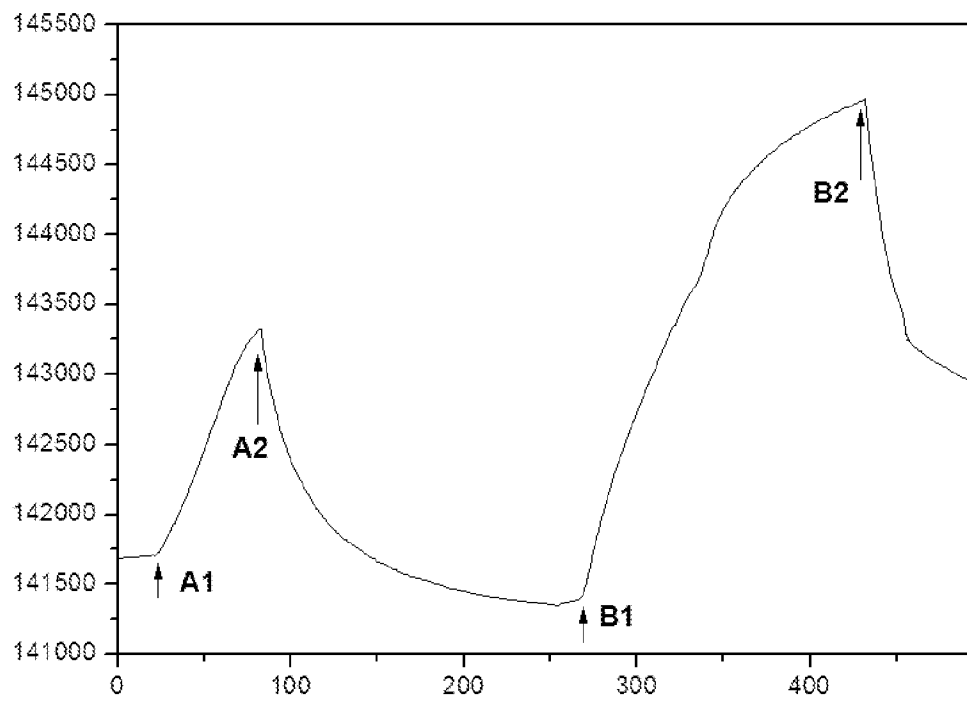


Fig. 6

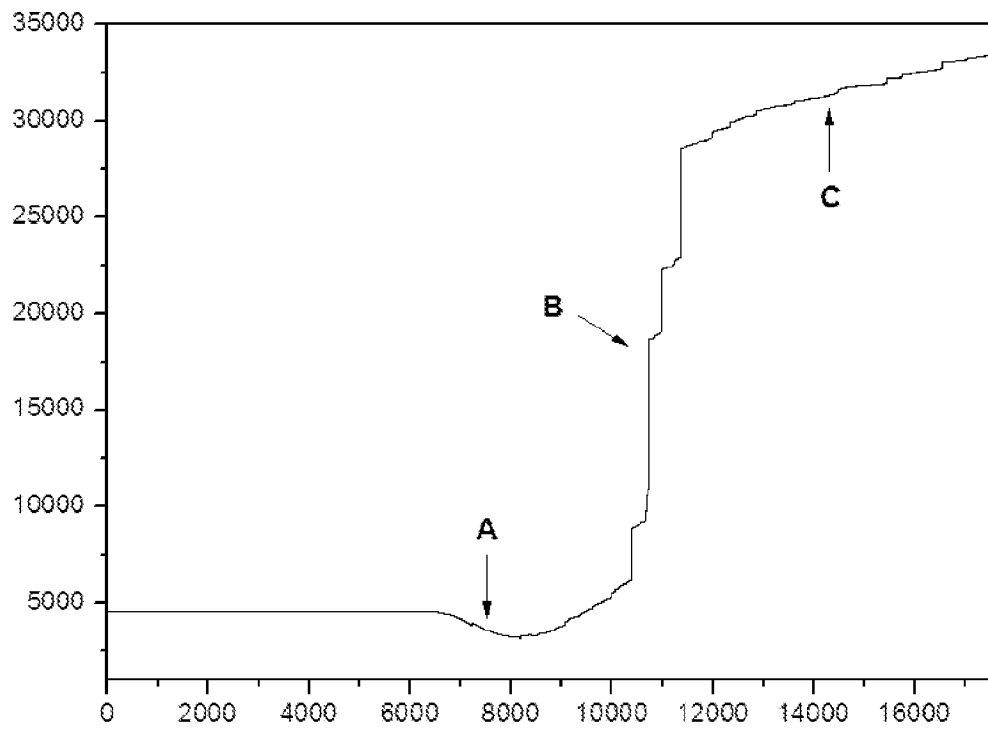
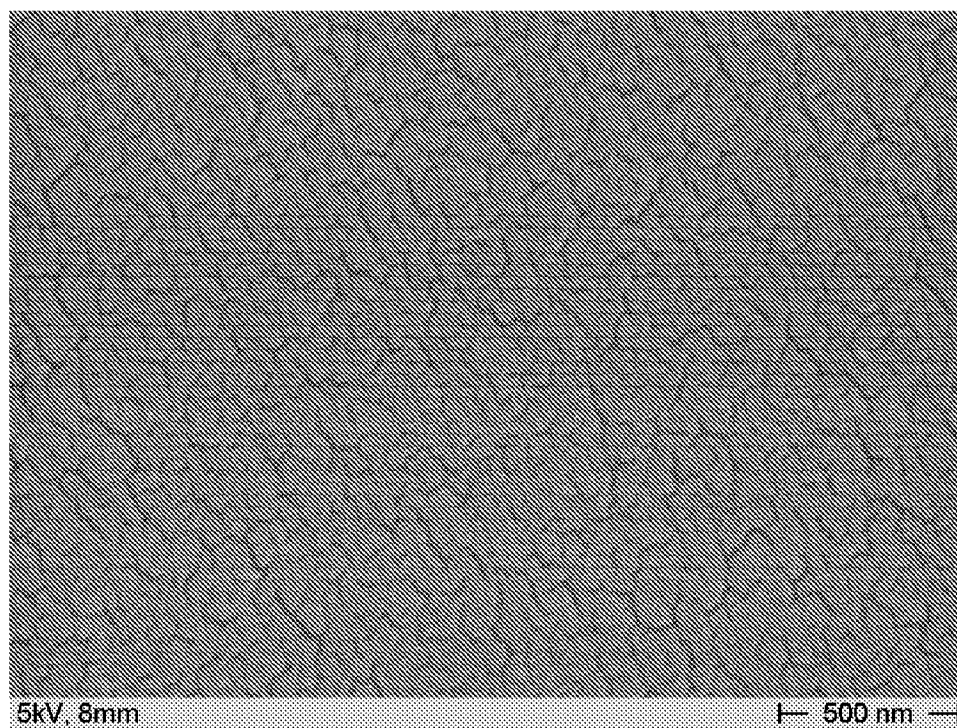
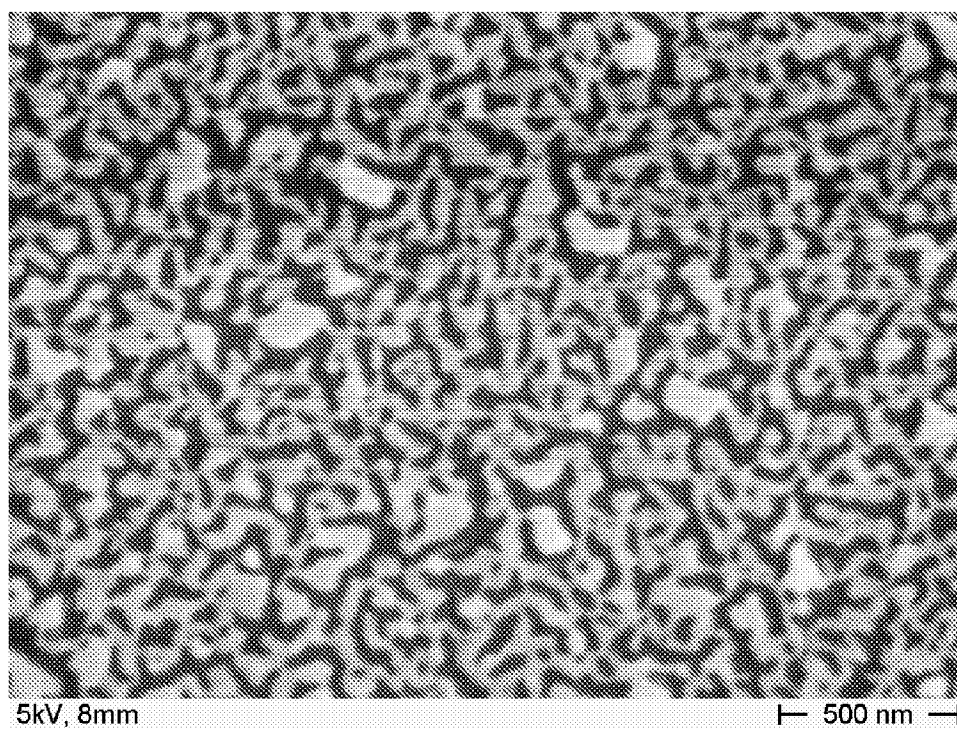
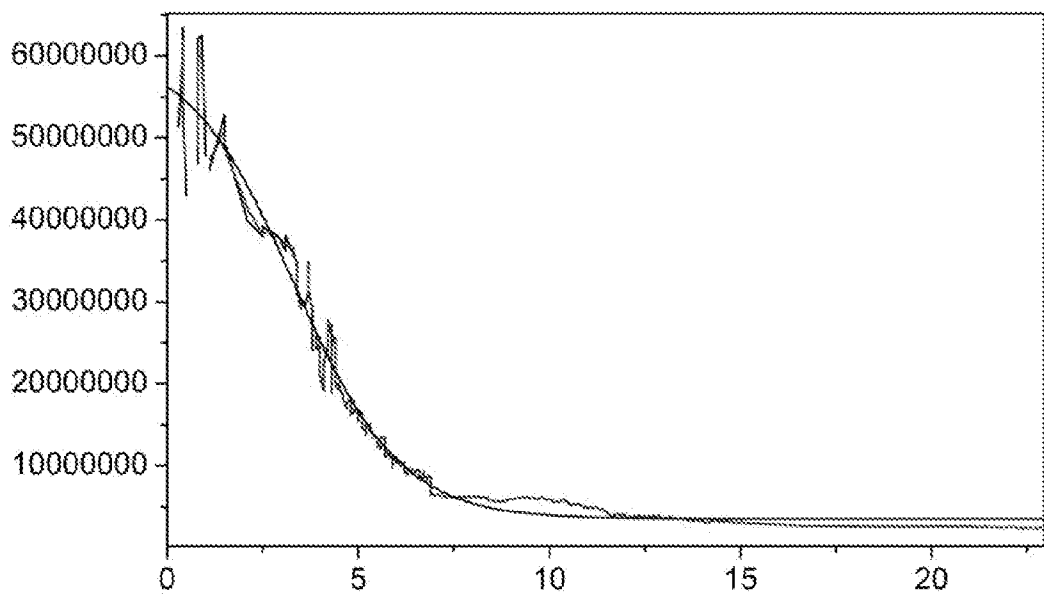
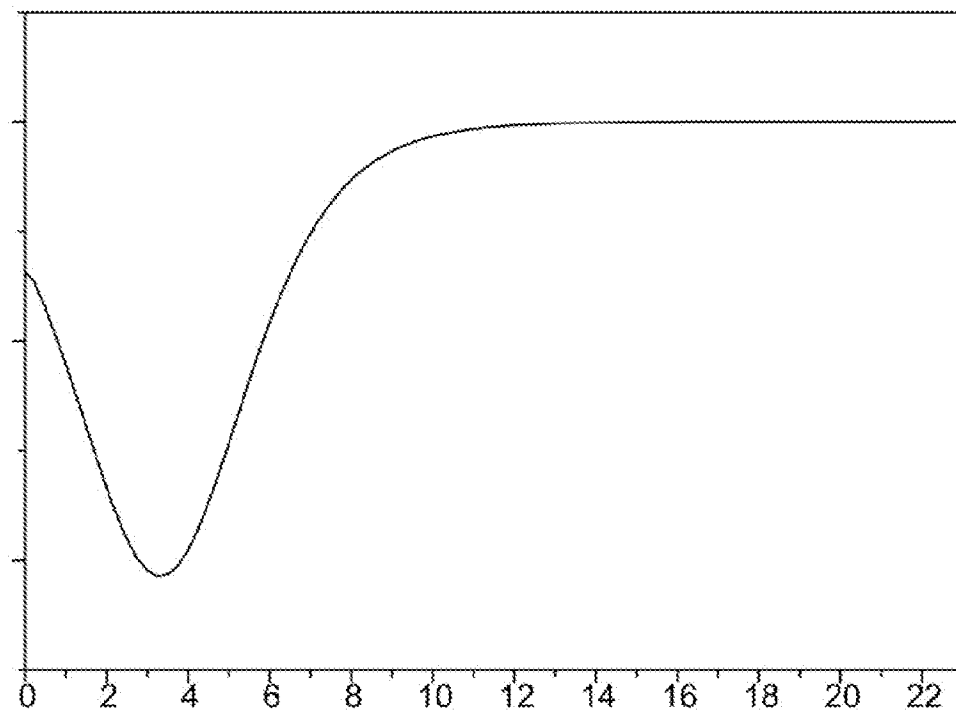
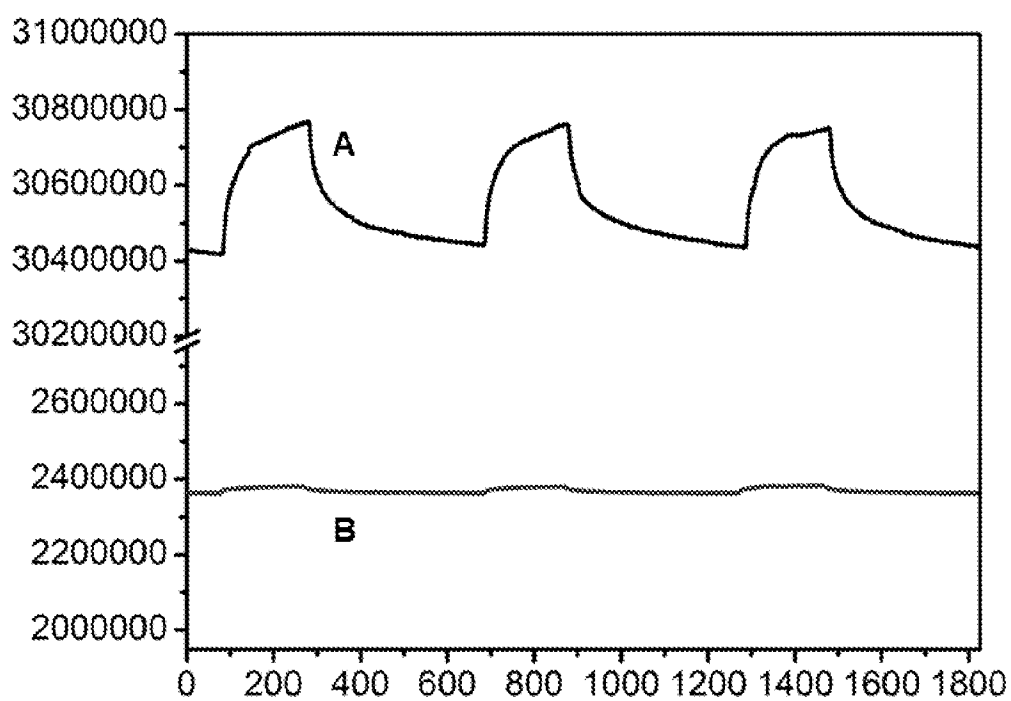
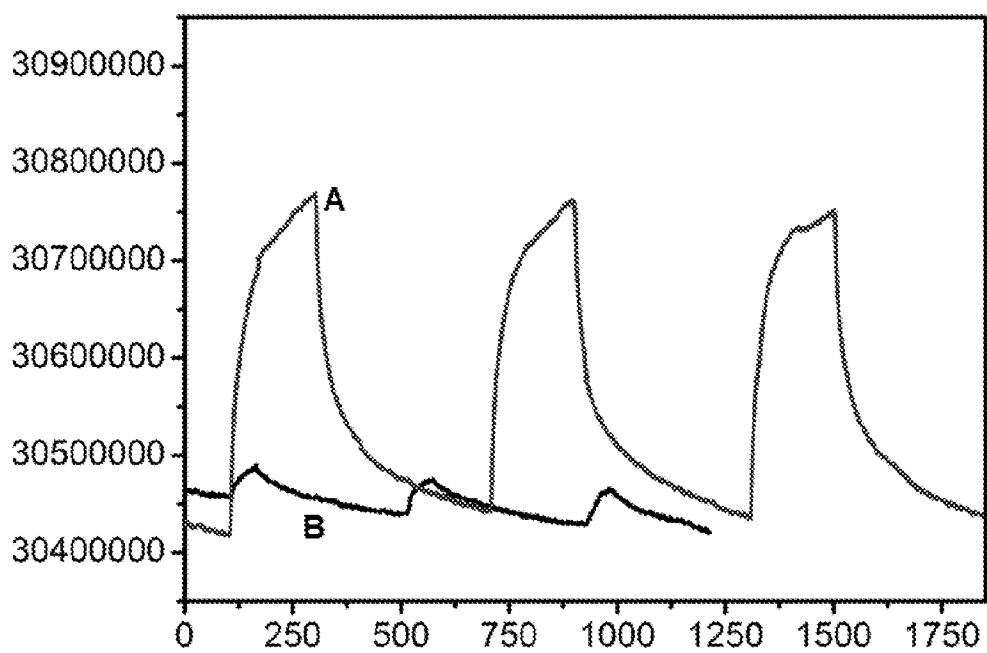


Fig. 7

**Fig. 8****Fig. 9**

**Fig. 10****Fig. 11**

**Fig. 12****Fig. 13**

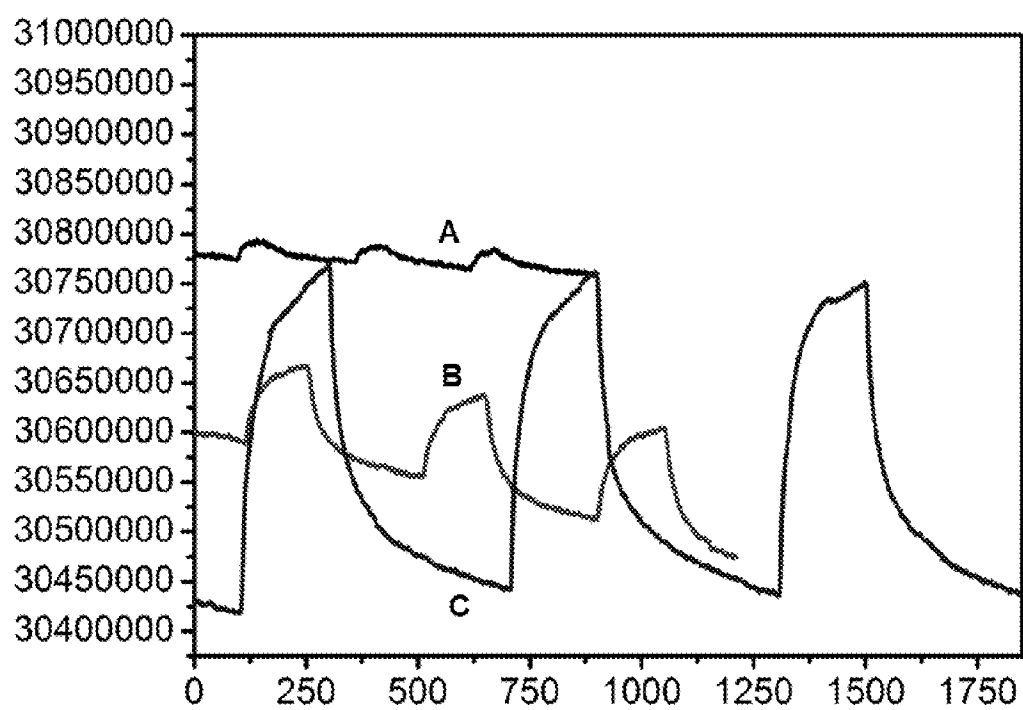


Fig. 14