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(54) Title: ORGANIC FIELD-EFFECT TRANSISTORS

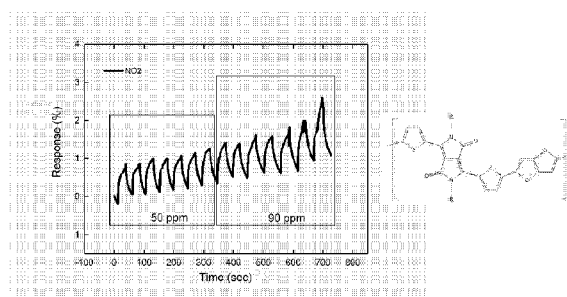


Fig. 3(a)

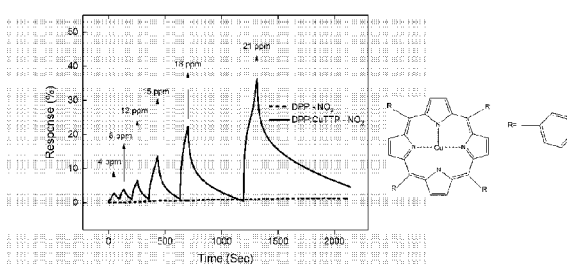


Fig. 3(b)

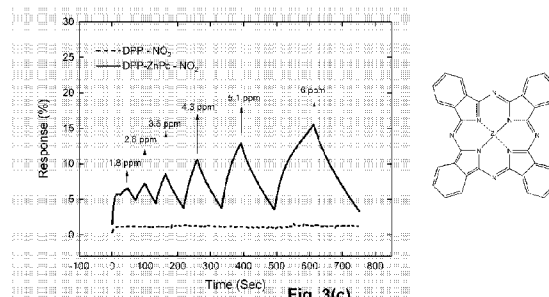


Fig. 3(c)

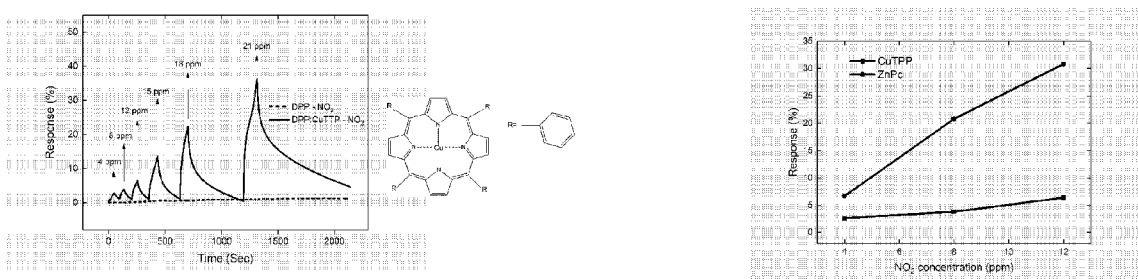


Fig. 3(d)

(57) **Abstract:** An organic field effect transistor (OFET) for use in a gas sensor for detecting the presence of one or more target gases, for example CO, CO₂, NO, NO₂, SO₂ or O₃. The OFET comprises a semiconducting layer arranged between a source electrode and a drain electrode, and additionally comprises a dielectric layer and a gate arranged on a substrate. The semiconducting layer is formed of a semiconducting material, suitably a semiconducting polymer, and an additive, suitably a multi-dentate organic ligand, for sensitising the semiconducting material to the presence of said target gases. The sensitising additive is present in the semiconducting material in an amount of up to 10 wt%. The OFET is suitably unencapsulated and suitably provides a sensitive and selective gas sensor which is stable to continuous operation in air. A gas sensor comprising the OFET and a method of preparing the OFET are also disclosed.

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Organic Field-Effect Transistors

Field

The present invention relates to an organic field effect transistor, a semiconducting film composition, a gas sensor and a method of producing an organic field effect transistor. In particular the present invention relates to an organic field effect transistor wherein the semiconducting material comprises a sensitising additive that may increase the sensitivity and/or selectivity of the semiconducting material to a target gas.

Background

Organic field-effect transistors (OFETs) are field-effect transistors comprising an organic semiconductor material arranged in a channel between a source electrode and a drain electrode. Such OFETs have been used in a variety of applications such as displays, circuits, gas sensors and biosensors. OFETs are attractive for such applications due to their potentially high sensitivity, portability, flexibility and low cost, particularly compared to inorganic counterparts such as metal oxides.

OFETs have been prepared by techniques such as vacuum evaporation of small molecules, solution-casting of polymers or small molecules, and mechanical transfer of single-crystalline organic layers onto a substrate. These devices have been developed to realize low-cost, large-area electronic products and biodegradable electronics. OFETs have been fabricated with various device geometries.

The structure of such OFETs is typically a top or bottom gate arrangement. Bottom gate OFETs comprise a bottom gate arranged on a substrate (for example glass or a polymeric material), a dielectric layer arranged on the gate and the source, drain and semiconductor material arranged on top of the dielectric layer. The dielectric layer can be provided by silicon dioxide or an organic polymer, such as poly(methyl-methacrylate) (PMMA).

OFETs have been used in gas sensors to identify the presence and/or to quantify the level of target gas molecules in air monitoring and ventilation systems. Many target gas molecules are colourless and/or odourless which means that their presence is not easily identified, particularly at low levels which may still be harmful to people and to the environment. For example, it is desirable to detect the presence of CO in homes and workplaces to prevent carbon monoxide poisoning.

Gas detection is also possible using other methods, for example spectrometry and spectroscopy, gas chromatography and optical sensing. Such methods are often highly selective and sensitive to specific target molecules. However, in most cases, these techniques

require expensive equipment and/or a high level of expertise is needed, which limits their use in real-time monitoring.

Known OFETs may be able to identify and/or quantify the presence of low levels of some gases, for example levels below 35 parts per million (ppm). However, such sensitive OFETs are not stable during operation in air under ambient conditions which severely restricts their usefulness in gas sensing applications.

Summary of the Invention

It is one aim of the present invention, amongst others, to provide an organic field effect transistor, gas sensor or method that addresses at least one disadvantage of the prior art, whether identified here or elsewhere, or to provide an alternative to existing organic field effect transistors. For instance it may be an aim of the present invention to provide an organic field effect transistor which can be used in gas sensors to detect the presence of gases at low concentrations.

According to aspects of the present invention, there is provided an organic field effect transistor, method, gas sensor and use as set forth in the appended claims. Other features of the invention will be apparent from the dependent claims, and the description which follows.

According to a first aspect of the present invention, there is provided an organic field effect transistor comprising a semiconducting layer arranged between a source electrode and a drain electrode; wherein the semiconducting layer comprises a semiconducting material and a sensitising additive; and wherein the sensitising additive is present in the semiconducting material in an amount of up to 10 wt%.

The organic field effect transistor of this first aspect is suitably used in a gas sensor to detect the presence of low concentrations of a target gas in a gaseous mixture, for example in air. The inventors have found that organic field effect transistors (OFETs) of this first aspect may have improved sensitivity to target gases (or analytes) present at low concentrations compared to known OFETs, for example similar OFETs which do not comprise the sensitising additive. For example, the OFET may be able to detect the presence of gases present at levels below 500 parts per billion (ppb), which may be useful in air quality monitoring applications.

The semiconducting layer provides a semiconducting electrical pathway between the source and drain electrodes and has a surface which can be exposed to a sample gas to be analysed, in use. Gas molecules from such a sample gas are able to permeate or be absorbed into the semiconducting layer through the surface, with the intention that the certain target gases in said sample gas produce a detectable change in the conduction of electricity through the semiconducting layer, which can in turn allow said target gas to be detected and/or quantified by the OFET.

The sensitising additive is suitably mixed into the semiconducting material in the semiconducting layer and is therefore distributed homogeneously throughout the semiconducting layer. The sensitising additive is suitably capable of binding to or otherwise interacting with a target gas molecule, when said target gas molecule is absorbed into the semiconducting layer as described above, and is capable of altering the electrical properties of the semiconducting material to a greater extent than the same target gas in the same semiconductor material which does not comprise the sensitising additive. The sensitising additive may be additionally or alternatively defined as a sensing additive or gas-binding or gas-detecting compound.

Without being bound by theory, it is believed that the sensitising additive binds to a target gas molecule in the semiconducting layer and changes the charge transfer properties of the semiconducting layer, therefore allowing the detection of the presence and/or concentration of said target gas through measurement of the change in conduction through the semiconducting layer.

The sensitising additive comprising said gas molecule may act as a charge trap to reduce conduction through the semiconducting layer. The sensitising additive itself may act as a charge trap to alter (either reduce or improve) conduction through a particular semiconducting material, compared to the same semiconducting material which does not comprise the sensitising additive. In such cases, for example wherein the target gas is CO or SO₂ (i.e. non-oxidising) the binding of said target gas molecule to the sensitising additive may change the extent to which the sensitising additive acts as a charge trap to alter conduction through the semiconducting layer, and it is therefore measuring this change which allows detection of said gas molecules.

Wherein the target gas is an oxidising gas (such as NO₂ and O₃), the conductivity of the OFET may increase during exposure to the target gas. Such oxidising gases may diffuse into the semiconducting layer and displace absorbed species such as oxygen, creating charge carriers (holes) in the semiconducting layer by charge (electron) transfer between the target gas and the sensitising additive. Since the organic semiconductor (DPPTTT) and the sensitising additives are p-type, the increase in hole charge carriers leads to an increase in their electrical conductivity.

The semiconductor material is suitably sensitive to certain target gases, without the presence of the sensitising additive. Therefore suitable semiconductor materials are able to have their charge transfer properties altered by the presence of absorbed target gas in the material and are therefore able to be used to detect the presence of said target gas by measuring this change in charge transfer properties. However, the inventors have found that the use of the sensitising additive in the semiconducting material in an amount of up to 10 wt% increases the sensitivity of the semiconducting material to target gases by producing a larger change in the

charge transfer properties of the semiconducting material for the same concentration of target gas present compared to the same semiconducting material without the sensitising additive. This may allow the OFET of this first aspect to detect lower concentrations of target gases than OFETs which do not comprise such sensitising additives are able to. Therefore the OFET of the first aspect may be particularly useful in gas monitoring applications for toxic gases, for example in air quality monitoring where low levels of toxic gases be harmful to people and/or the environment and therefore their detection and/or quantification is important.

The semiconducting layer is suitably air stable. This suitably allows the OFET of this first aspect to be unencapsulated. The OFET is suitably unencapsulated. Such air stable unencapsulated OFETs are much more useful in practical applications of air monitoring than encapsulated, air sensitive OFETs, which rapidly degrade on expose to air in use. Suitably the OFET is stable to operation in air.

This first aspect suitably provides an OFET transistor comprising a semiconducting layer arranged between a source electrode and a drain electrode; wherein the semiconducting layer comprises a semiconducting material and a sensitising additive; wherein the sensitising additive is present in the semiconducting material in an amount of up to 10 wt%; wherein the sensitising additive comprises a metal selected from one or more of chromium, manganese, iron, cobalt, nickel, copper, zinc, silver and cadmium; suitably wherein the OFET is stable to operation in air.

The semiconducting layer of the first aspect comprises a semiconducting material. The semiconducting material is suitably a solid, stable material, suitably an organic material. The semiconducting material may be a small molecule, an oligomeric or a polymeric semiconducting material. Suitably the semiconducting material is a polymeric semiconducting material (i.e. a semiconducting polymer). Suitably the semiconducting material is a semiconducting polymer. Suitably the semiconducting material is an air stable polymeric semiconducting material. Suitably the air stable polymeric material has an ionisation potential of greater than 5 eV. For example, the semiconducting material may be poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene) (DPPTTT), which is considered to be air stable. In some embodiments, the semiconducting material may be selected from 6,6'-dithienylindigo (DTI) and derivatives, 10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole (triindole) and derivatives or bistetracene.

Other suitable semiconducting materials may be known to those skilled in the art.

Suitably the semiconducting material is not an air unstable polymer, for example poly(3-hexylthiophene) (P3HT). Suitably the semiconducting material does not have an ionisation potential of below 5 eV.

The semiconducting material may be a blend of a polymeric semiconducting material and a second polymer. The second polymer may not be a semiconducting polymer, but suitably the polymeric semiconducting material retains its semiconducting properties when blended with the second polymer. The second polymer suitably functions to improve the stability of the semiconductor layer to long term bias stress. For example, when DPPTTT is used as the polymeric semiconducting material, the semiconducting layer may suffer from degradation in electrical properties over time under bias stress. If a second polymer such as PMMA or poly(alpha-methylstyrene) (PAMS) is blended with the DPPTTT, the resultant semiconducting layer may have improved stability under bias stress. Suitably the semiconducting material comprises at least 10 wt% of the second polymer, suitably at least 20 wt%. Suitably the semiconducting material comprises up to 50 wt% of the second polymer, suitably up to 40 wt%, for example approximately 30 wt%. In some embodiments, the semiconducting material comprises from 60 to 80 wt% of DPPTTT and from 20 to 40 wt% PMMA or PAMS, suitably PMMA. Other polymers may be suitable as the second polymer in the semiconducting material, for example polymers which promote phase separated structures such as polystyrene and other similar materials. Such polymers may be selected from acrylates, styrenics, soluble polyesters and polyamides. Suitably the second polymer and the semiconducting polymer are both soluble in a particular solvent in order to facilitate their mixing and formation of the semiconducting material.

This first aspect suitably provides an OFET transistor comprising a semiconducting layer arranged between a source electrode and a drain electrode; wherein the semiconducting layer comprises a semiconducting material and a sensitising additive; wherein the sensitising additive is present in the semiconducting material in an amount of up to 10 wt%; wherein the sensitising additive comprises a metal selected from one or more of chromium, manganese, iron, cobalt, nickel, copper, zinc, silver and cadmium; wherein the semiconducting material comprises from 60 to 80 wt% of DPPTTT and from 20 to 40 wt% PMMA; suitably wherein the OFET is stable to operation in air.

The semiconducting layer comprises the semiconducting material and the sensitising additive; the sensitising additive being present in the semiconducting material in an amount of up to 10 wt%. Suitably the sensitising additive is or comprises a sensitising compound which can bind to or interact with a target gas molecule such as CO, CO₂, NO, NO₂, SO₂ or O₃. This interaction can be chemical or physical and includes hydrogen bonding, permanent dipole-dipole interactions and Van der Waal interactions. Suitably the binding or interaction alters the extent to which the sensitising additive affects the charge transfer properties of the semiconducting material, as discussed above.

Suitably the sensitising additive is a compound which can bind to a metal atom to form a sensitising complex, for example a compound which can bind to a transition metal such as chromium, manganese, iron, cobalt, nickel, copper, zinc, silver and cadmium. Suitably the

sensitising additive comprises a metal. Therefore the sensitising additive is suitably a sensitising complex comprising a sensitising compound and a metal, wherein the metal is bound to or ligated by the sensitising compound and wherein a target gas molecule can bind to the metal. The metal may be selected from any of the transition (d-block) metals and aluminium. Suitably the metal is a transition metal. Suitably the metal is a transition metal from the first row of the periodic table of elements. The metal is suitably selected from one or more of chromium, manganese, iron, cobalt, nickel, copper, zinc, silver and cadmium. Suitably the metal is one of either chromium, manganese, iron, cobalt, nickel, copper, zinc, silver or cadmium.

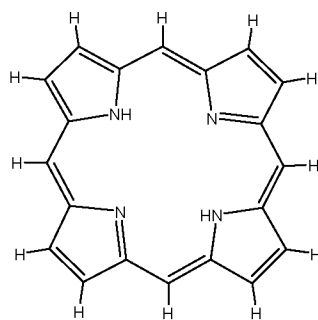
10 In some embodiments, the metal is selected from copper, iron and zinc.

Suitably the sensitising additive is or comprises an organic ligand comprising at least one heteroatom and is suitably capable of binding to a metal, as described above. Suitably such an organic ligand is a multi-dentate ligand comprising more than one heteroatom, suitably having a rigid framework. Suitably the heteroatom or heteroatoms is/are selected from nitrogen, oxygen and sulphur.

Such organic ligands may be or comprise a macrocycle. For example, the sensitising additive may be or comprise a cyclic molecule selected from a porphyrin, a phthalocyanine or a crown ether. Suitably the sensitising additive comprises a porphyrin or a phthalocyanine.

In some embodiments, the sensitising additive is or comprises a porphyrin compound.

20 Porphyrins comprise four pyrrole subunits interconnected by methine bridges as shown in structure (I) below.

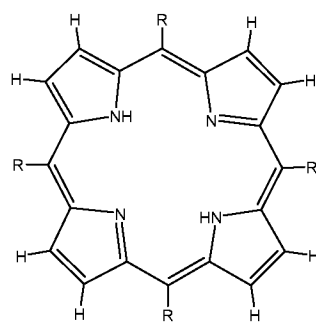


(I)

Suitably the sensitising additive is a porphyrin or a derivative thereof. A suitable porphyrin derivative may be a porphyrin according to structure (I) comprising one or more substituents in place of the hydrogens, for example benzoporphyrin, tetraphenylporphyrin or an expanded porphyrin.

Suitable substituents may be hydrocarbyl groups. As used herein, the term "hydrocarbyl" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

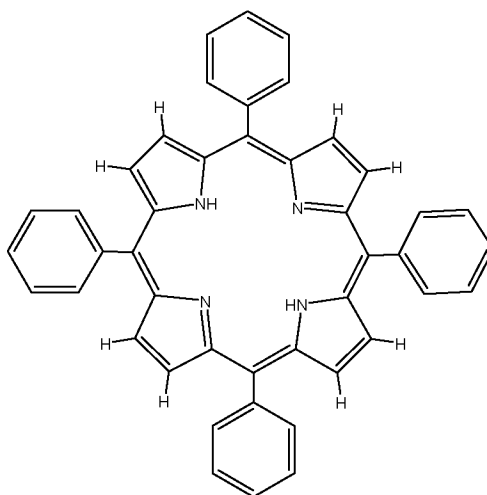
- 5 (i) hydrocarbon groups, that is, aliphatic (which may be saturated or unsaturated, linear or branched, e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);
- 10 (ii) substituted hydrocarbon groups, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, keto, acyl, cyano, mercapto, alkylmercapto, amino, alkylamino, nitro, nitroso, and sulphony);
- 15 (iii) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulphur, oxygen, nitrogen and encompass substituents such as pyridyl, furyl, thienyl and imidazolyl.
- 20 Suitably the sensitising additive comprises a porphyrin compound according to structure (II) below.



(II)

Suitably R represents a hydrocarbyl group as defined above.

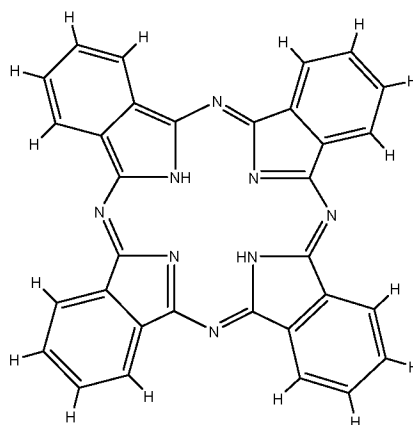
- 25 Suitably the sensitising additive is 5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrin (TPP), shown in structure (III) below.



(III)

In some embodiments the sensitising additive is or comprises an expanded porphyrin. Expanded porphyrins comprise more than four pyrrole subunits interconnected by methine bridges. For example, the sensitising additive may be or comprise an expanded porphyrin comprising at least five, for example at least six pyrrole subunits. Such expanded porphyrins may comprise substituents in place of the hydrogen atoms as described above, suitably hydrocarbyl substituents.

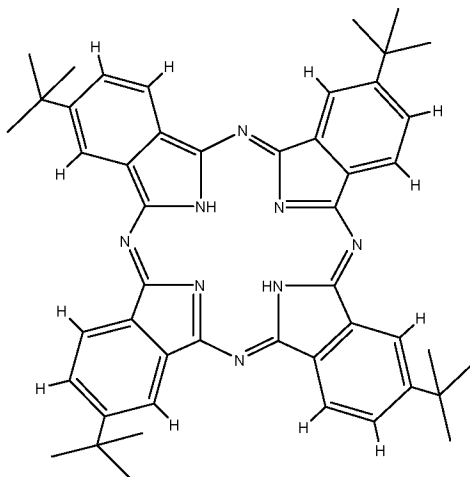
In some embodiments, the sensitising additive is or comprises a phthalocyanine compound. Phthalocyanine comprises nitrogen-linked tetramic diiminoisoindoline units as shown in structure (IV) below.



(IV)

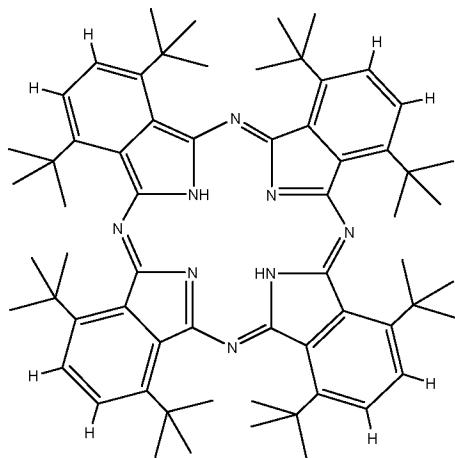
Suitably the sensitising additive is a phthalocyanine or a derivative thereof, for example a phthalocyanine according to structure (IV) comprising one or more substituents, in place of the hydrogens. Suitably the substituents may be hydrocarbyl groups as defined above. For example the phthalocyanine sensitising additive may comprise 2,9,16,23-tetra-*tert*-butyl-

29*H*,31*H*-phthalocyanine (TTB), as shown in structure (V) below, suitably with a metal, for example zinc.



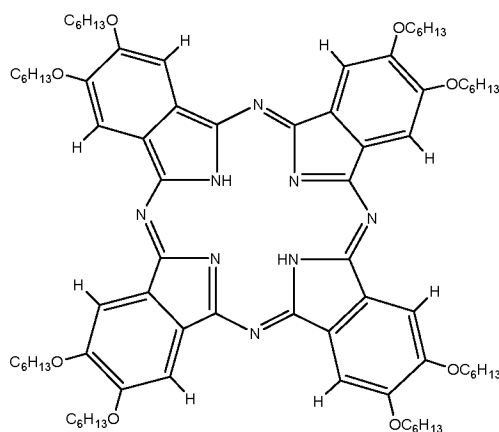
(V)

- 5 Suitably the substituents on the phthalocyanine may be an alkyl group, for example a methyl or ethyl group. Suitably the substituents include tetramethyl groups. For example, the phthalocyanine sensitising additive may be a compound of formula (VI).



(VI)

- 10 The substituent may include a heteroatom, for example an oxygen atom. The substituent may form an ether linkage. For example, the phthalocyanine sensitising additive may be a compound of formula (VII).



(VII)

In some embodiments, the sensitising additive is or comprises a crown ether. Crown ethers comprise several ether groups connected in a ring. For example the sensitising additive may be selected from 12-crown-4, 15-crown-5, 18-crown-8 and derivatives thereof.

In some embodiments, the sensitising additive comprises an organic ligand comprising at least one heteroatom as described above, for example a porphyrin, a phthalocyanine or a crown ether, and a metal as described above. For example, the sensitising additive may comprise a porphyrin, a phthalocyanine or a crown ether, and a metal selected from one or more of chromium, manganese, iron, cobalt, nickel, copper, zinc, silver and cadmium. Suitably the sensitising additive comprises a porphyrin or a phthalocyanine, and a metal selected from one or more of chromium, manganese, iron, cobalt, nickel, copper, zinc, silver and cadmium. Suitably the sensitising additive comprises a porphyrin or a phthalocyanine, and a metal selected from iron, copper and zinc.

In some embodiments the sensitising additive is 5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrin copper (II). This sensitising additive may be referred to as CuTPP.

In some embodiments the sensitising additive is zinc phthalocyanine. This sensitising additive may be referred to as ZnPc.

In some embodiments the sensitising additive is iron phthalocyanine. This sensitising additive may be referred to as FePc.

In some embodiments the sensitising additive is zinc 2,9,16,23-tetra-*tert*-butyl-29*H*,31*H*-phthalocyanine (TTB). This sensitising additive may be referred to as TTB-ZnPc.

In some embodiments, the sensitising additive is a phthalocyanine compound of formula (VI) or formula (VII), without a metal present (i.e. a “metal free” sensitising additive).

The semiconducting layer comprises the sensitising additive in an amount of up to 10 wt%, suitably up to 8 wt% or up to 6 wt%. Suitably the sensitising additive is present in the semiconducting material in an amount of up to 5 wt%, for example up to 3 wt% or up to 1.1 wt%.

- 5 Suitably the sensitising additive is present in the semiconducting material in an amount of at least 0.01 wt%, for example at least 0.1 wt% or at least 0.2 wt%. Suitably the sensitising additive is present in the semiconducting material in an amount of at least 0.5 wt%, suitably at least 0.7 wt%, for example at least 0.9 wt %.

- 10 Suitably the sensitising additive is present in the semiconducting material in an amount of from 0.01 wt% to 10 wt%, for example from 0.1 wt% to 5 wt%. Suitably the sensitising additive is present in the semiconducting material in an amount of from 0.1 wt% to 2 wt%. Suitably the sensitising additive is present in the semiconducting material in an amount of from 0.5 to 1.5 wt%, for example about 1 wt%.

- 15 Alternatively the amount of sensitising material may be defined in terms the ratio of semiconducting material : sensitising additive. Suitably the ratio of semiconducting material : sensitising additive is up to 100 : 10 for example up to 100 : 8 or up to 100 : 6. Suitably the ratio of semiconducting material : sensitising additive is up to 100 : 4, for example up to 100 : 2, for example approximately 100 : 1.

- 20 Suitably the ratio of semiconducting material : sensitising additive is at least 100,000 : 1, suitably at least 10,000 : 1 for example at least 1,000 : 1 or at least 1,000 : 5.

Suitably the ratio of semiconducting material : sensitising additive is from 10,000 : 1 to 100 : 10, suitably from 1,000 : 1 to 100 : 10, suitably from 1,000 : 5 to 100 : 5.

- 25 Suitably the semiconducting material and the sensitising additive provide at least 80 wt% of the semiconducting layer, suitably at least 90 wt%, suitably at least 95 wt%, suitably at least 98 wt% or at least 99 wt% or at least 99.9 wt% of the semiconducting layer. Suitably the semiconducting layer consists essentially of the semiconducting material and the sensitising additive. Suitably the semiconducting layer consists of the semiconducting material and the sensitising additive.

- 30 The inventors have found that inclusion of the sensitising additive in the semiconducting material in amount of up to 10 wt% may improve the sensitivity of the semiconducting layer for detecting lower levels of target gases. Including the sensitising additive in amounts greater than 10 wt% may significantly reduce the performance of the OFET when used to detect relatively low concentrations of target gas.

Suitably the target gas which the OFET is intended to detect the presence of in use is a small gaseous molecule, suitably selected from CO, CO₂, SO₂, O₃ and NO_x. As is known in the art, NO_x refers to compounds NO and NO₂.

5 The inclusion of the sensitising additive in the semiconducting material suitably allows for the detection of low levels of such target gases. By "low levels" we mean to refer to levels of 50 parts per million (ppm), for example 10 ppm. Suitably the OFETs of this first aspect allow for the detection of target gases in a gaseous mixture (suitably air) at a concentration of 1 ppm, suitably 500 ppb or 250 ppb, suitably 200 ppb, for example 150 ppb. Suitably the OFETs of this first aspect allow for the detection of target gases in a gaseous mixture (suitably air) at a
10 concentration of 100 ppb, suitably 50 ppb, suitably 10 ppb or 1 ppb.

Suitably the semiconducting layer has a thickness of up to 200 nm, suitably up to 150 nm or up to 100 nm, for example up to 50 nm. Suitably the semiconducting layer has a thickness of at least 5 nm, suitably at least 10 nm or at least 20 nm. Suitably the semiconducting layer has a thickness of from 5 nm to 200 nm, for example from 10 nm to 100 nm or from 10 nm to 50 nm.

15 Besides the semiconducting material and the source and drain electrodes discussed above, the other typical components of such OFETs would be known to those skilled in the art, for example the suitable arrangements of the source and drain electrodes and the semiconducting material on the dielectric, gate and substrate described above. Suitably the OFET of this first aspect is a bottom gate OFET wherein the source and drain electrodes and the
20 semiconducting material are arranged on and in contact with a dielectric layer, wherein the dielectric layer is arranged on and in contact with a gate and wherein the gate is arranged on and in contact with a substrate.

The substrate supports the layers above. Suitably the substrate is a polymeric material, suitably a polymeric film. Suitable polymeric materials may be selected from polyethylene
25 terephthalate (PET), polyethylene naphthalate (PEN), polyether ether ketone, polyphenylene sulfide, polyarylate, polyimide, polycarbonate (PC), cellulose triacetate (TAC), or cellulose acetate propionate (CAP). The substrate is suitably polyethylene naphthalate (PEN). The use of such polymeric films may reduce the weight and improve the flexibility of the OFET compared to other substrates.

30 Suitably the OFET comprises a gate electrode. Suitably the gate electrode comprises a conductive material, for example gold, silver, aluminium, copper, chromium, nickel, cobalt, titanium and platinum.

Suitably the gate electrode has a thickness of from 20 nm to 500 nm, suitably from 30 nm to 300 nm. Suitably the gate electrode has a thickness of approximately 70 nm.

The OFET suitably comprises a dielectric layer. The dielectric layer may additionally or alternatively be described as a gate-insulating layer.

Suitably the dielectric layer comprises polymers such as polymethyl methacrylate, polystyrene, polyvinyl phenol, polyvinylidene, polyimide, polycarbonate, polyester, polyvinyl alcohol, polyvinyl acetate, polyurethane, polysulfone, polybenzo-oxazole, polysilsesquioxane, epoxy resins and phenolic resins, and derivatives thereof; oxides such as silicon monoxide, silicon dioxide, aluminium oxide, and titanium oxide and nitrides such as silicon nitride.

Suitably the dielectric layer comprises a mixture of polymeric materials. Suitably the dielectric layer comprises a high-k dielectric polymer material and a low-k dielectric polymer material.

Suitably the dielectric layer comprises a polyvinylidene derivative and polymethyl methacrylate (PMMA). Suitably the dielectric layer comprises a layer of a polyvinylidene derivative and a layer of polymethyl methacrylate, suitably on top of the polyvinylidene derivative. Suitably the high-k dielectric polymer material is vinylidene fluoride-trifluoroethylene-chlorofluoroethylene terpolymer and the low-k dielectric polymer material is poly(methyl methacrylate). A relatively thin layer (approximately 30 nm) of low-k polymer (such as PMMA) on the high-k polymer dielectric film may improve the long term, bias stress stability of the dielectric layer, by reducing the effect of underlying dipoles and surface polarity.

The OFET comprises source and drain electrodes. The source and drain electrode are suitably rectangular electrodes. The source and drain electrodes are arranged such that a semiconducting layer can be placed in between them. Suitably there is a channel between the source and drain electrodes in which the semiconducting material can be placed.

As with the gate electrode, any suitable conducting material may be used to form the source and drain electrodes. Suitably the source and drain electrodes comprise gold. Suitably the source and drain electrodes comprise gold that has been pre-treated with a self-assembled monolayer solution.

The OFET may be considered to be a composition comprising the semiconducting layer comprising the sensitising additive, suitably a relatively thin composition, for example having a thickness of from 125 to 130 μm . The thickness of the semiconducting layer may be from 10 to 200 nm.

The OFET may also be considered to be a coating. The OFET is suitably arranged on a substrate and is a relatively thin coating on said substrate, compared with the thickness of said substrate. Suitable substrates are glass or plastic.

Suitably the OFET of this first aspect is flexible and/or printable onto a substrate, suitably a flexible substrate.

Suitably the OFET of this first aspect can be produced and/or arranged onto a substrate without the use of inert atmospheres or "clean room" conditions.

According to a second aspect of the present invention, there is provided a semiconducting film composition comprising a semiconducting material and a sensitising additive; wherein the
5 sensitising additive is present in the semiconducting material in an amount of up to 10 wt%.

The semiconducting film composition, the semiconducting material and the sensitising additive may have any of the suitable features and advantages described in relation to the first aspect.

According to a third aspect of the present invention, there is provided a gas sensor comprising an organic field effect transistor of the first aspect.

10 Suitably the semiconducting layer of the OFET of the gas sensor is sensitive to CO, CO₂, NO, NO₂, SO₂ or O₃. In other words, the semiconducting layer changes its charge transfer properties on exposure to said gases, through interaction of said gases with the sensitising additive in the semiconducting layer, as described in relation to the first aspect.

Suitably the gas sensor of this third aspect is operable to detect CO, CO₂, NO, NO₂, SO₂ or O₃
15 present in a gaseous mixture (suitably air) at a concentration of 50 ppm, for example 10 ppm. Suitably the gas sensor is operable to detect said target gases in a gaseous mixture (suitably air) at a concentration of 1 ppm, suitably 500 ppb or 250 ppb, suitably 200 ppb, for example 150 ppb. Suitably the gas sensor is operable to detect said target gases in a gaseous mixture (suitably air) at a concentration of 100 ppb, suitably 50 ppb, suitably 10 ppb or 1 ppb.

20 Suitably the gas sensor may be used to monitor the presence and/or levels of toxic gases. For example the gas sensor may be used to monitor the presence and/or levels of NO, NO₂, SO₂ and CO.

Suitably the gas sensor of the third aspect is used in atmospheric monitoring, for example in safety devices to detect the presence of CO in homes and workplaces.

25 According to a fourth aspect of the present invention, there is provided a use of a multi-dentate organic ligand to improve the sensitivity of a semiconducting material in an organic field effect transistor to a target gas.

Suitably the use of this fourth aspect improves the sensitivity of the semiconducting material to target gases (or analytes) present at low concentrations compared to known OFETs, for
30 example similar OFETs which do not comprise the sensitising additive. For example, the semiconducting material may be able to detect the presence of gases present at levels below 500 parts per billion (ppb), which may be useful in air quality monitoring applications.

The multi-dentate organic ligand (sensitising additive), the semiconducting material and the organic field effect transistor may have any of the suitably features and advantages described in relation to the first aspect.

According to a fifth aspect of the present invention, there is provided a method of preparing an organic field effect transistor, the method comprising the steps of:

- a) depositing a gate electrode onto a substrate;
- b) depositing a dielectric layer onto the gate electrode;
- c) depositing a capping layer onto the dielectric layer;
- d) depositing source and drain electrodes onto the dielectric layer; and
- 10 e) depositing a semiconducting layer onto the source and drain electrodes;

wherein the semiconducting layer comprises a semiconducting material and a sensitising additive, wherein the sensitising additive is present in the semiconducting material in an amount of up to 10 wt%.

Suitably the gate electrode, dielectric layer, source electrode, drain electrode and semiconducting layer are as described in relation to the first aspect.

Suitably the steps of the method are carried out in the order of step a) followed by step b) followed by step c) followed by step d) followed by step e).

Suitably the substrate is a flexible polymeric material, suitably polyethylene naphthalate (PEN).

Suitably the substrate in step a) is cleaned prior to depositing the gate electrode. For example the substrate may be cleaned with isopropanol and dried. The substrate may undergo further processing, for example UV-ozone treatment.

Suitably the gate electrodes are deposited onto the substrate in step a) using a thermal evaporation method.

The dielectric layer may be deposited onto the gate electrode in step b) using a spin coating process, suitably followed by annealing. The dielectric layer is suitably formed from a high-k polymer.

Step c) involves depositing a capping layer onto the dielectric layer. The capping layer is suitably deposited using spin coating, suitably followed by annealing. The capping layer is suitably formed of a low-k polymer, for example PMMA.

Depositing the source and drain electrodes of step d) may be carried out simultaneously. Suitably the source and drain electrodes may be deposited using a thermal evaporation method.

5 Suitably, prior to step e) the source and drain electrodes are treated with a self-assembled monolayer solution. For example, wherein the source and drain electrodes are gold electrodes, said electrodes may be treated with a thiol, suitably pentafluorothiophenol.

The semiconducting layer may be deposited on the source and drain electrodes using spin coating. The semiconducting layer may be annealed in a nitrogen environment.

10 The organic field effect transistor produced by the method of this fifth aspect may have any of the suitable features and advantages of the organic field effect transistor described in the first aspect.

Suitably the organic field effect transistor produced by the method of this fifth aspect is an organic field effect transistor of the first aspect.

Examples

15 Materials

Zinc phthalocyanine (ZnPc), zinc 2,9,16,23-tetra-tert-butyl-29H,31H-phthalocyanine (TTB-ZnPc), iron phthalocyanine (FePc), 5,10,15,20-tetraphenyl-21H,23H-porphine copper(II) (CuTPP), poly(methyl methacrylate) (PMMA, with molecular weight 120,000, 99.9% purity) and benzophenone were purchased from Sigma-Aldrich. Terpolymer (poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene, P(VDF-TrFE-CFE), 100% purity) was
20 purchased from Piezotech Inc. All solvents (99% purity) were purchased from Sigma-Aldrich.

Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene) (DPPTTT, also sometimes referred to as DPP) may be synthesised by the method described in Li, J.; Zhao, Y.; Tan, H.S.; Guo, Y.; Di, C.A.; Yu, G.; Liu, Y.; Lin, M.; Lim, S.H.;
25 Zhou, Y., et al. A stable solution-processed polymer semiconductor with record high-mobility for printed transistors. *Sci Rep* **2012**, 2, 754 (doi:10.1038/srep00754).

Metal-free phthalocyanines Pc1 (the compound of formula (IV) - 29H,31H-tetrabenzo[b,g,l,q]porphine) was prepared as described in S. Ito, T. Murashima, N. Ono and H. Uno, *Chem. Commun.*, 1998, **0**, 1661–1662.

30 Pc2 (the compound of formula (VII) - 2,3,9,10,16,17,23,24-octakis(hexyloxy)-29H,31H-tetrabenzo[b,g,l,q]porphine) was prepared as described in G. J. Clarkson, N. B. McKeown and K. E. Treacher, *J. Chem. Soc., Perkin Trans. 1*, 1995, 1817–7.

Preparation of OFETs

Comparative and Example OFETs were prepared on flexible PEN substrates as follows. The PEN substrates were bonded to glass substrates (24 × 24 mm²) using a cool-off tape. The substrates were thoroughly cleaned with isopropanol and dried at 80°C for 5 min, followed by UV-ozone treatment for 5 min. Aluminium (approximately 50 nm thick) gate electrodes were deposited using a shadow mask by thermal evaporation. Next, a high-k polymer solution was prepared by dissolving 5 wt% terpolymer in dimethyl formamide and was deposited onto the aluminium gate electrodes by spin coating.

The spin coating parameters were optimized (3000 rpm, 2 min) to obtain a thickness of 170±5 nm and the films were annealed at 110°C for 2 hours to evaporate the solvent and to crystallize the polymer. Next, a low-k polymer solution was prepared by dissolving 2 wt% PMMA with a photoinitiator (benzophenone) in anisole and was spin coated at 3000 rpm for 1 min to obtain a thickness of 30±5 nm. These films were dried at 80°C for 10 min and treated with a UV lamp (wavelength of 254 nm) for 10 min and annealed at 90°C for 30 min. Then 50 nm of gold electrodes (source and drain) were deposited using a shadow mask by thermal evaporation. The channel length and widths were fixed to 140 µm and 3,600 µm, respectively. Gold electrodes were treated with 2 mM 2,3,4,5,6-pentafluorothiophenol (PFBT) for 2 min and dried at 100°C for 5 min.

The semiconducting material for the formation of the semiconducting layer was prepared using a 5 mg/mL solution of DPPTTT in dichlorobenzene which was mixed with a 5 mg/mL solution of PMMA in dichlorobenzene in volumetric ratio of 70:30 to make a DPPTTT/PMMA solution. In the Example OFETs, the sensitising additives discussed below were added at this stage in the stated ratios compared to the amount of DPPTTT/PMMA.

Finally, the semiconducting layer was spin coated at 3000 rpm for 2 min and the films were annealed at 100°C for 1 hour under nitrogen.

A schematic of an OFET (100) prepared in this manner is shown in Figure 1 wherein gate 102 is arranged on substrate 101, dielectric layer 103 is arranged on gate 102, capping layer 104 is arranged on dielectric layer 103, source 105 and drain 106 electrodes are arranged on capping layer 104 and semiconducting layer 107 is arranged on the capping layer 104 between the source 105 and drain 106 electrodes.

Comparative Examples 0 and 1

Comparative Example 1 was prepared according to the method described above for the semiconducting layer without the addition of a sensitising additive. Comparative Example 0 was prepared by similar method without blending the DPPTTT with PMMA.

Examples 1-6

OFET Examples 1-6 (of the invention) were prepared as follows: in each example, the sensitising additive in dichlorobenzene (1 mg/mL) was added to the semiconducting material in various weight ratios (100:1, 100:2, 100:4, 100:10) and then used to form the semiconducting layer of the OFET as described above. The Examples 1-6 detailed below in Table 1 comprise a weight ratio of semiconducting material : sensitising additive of 100:1.

Table 1 – Example semiconducting layers

Example	Semiconducting material (1)	Sensitising additive (2)	Ratio of (1):(2)
CE 0*	DPPTTT	-	-
CE 1*	DPPTTT:PMMA (70:30)	-	-
1	DPPTTT:PMMA (70:30)	CuTPP	100:1
2	DPPTTT:PMMA (70:30)	ZnPc	100:1
3	DPPTTT:PMMA (70:30)	TTB-ZnPc	100:1
4	DPPTTT:PMMA (70:30)	FePc	100:1
5	DPPTTT:PMMA (70:30)	Pc1	100:1
6	DPPTTT:PMMA (70:30)	Pc2	100:1

*Comparative Examples comprising no sensitising additives.

The OFETs prepared as described above using the DPPTTT/PMMA semiconductor blend showed good stability under long bias stress, at different measurement temperatures and after one month of storage. Figure 2(a) shows the change in I_{DS} over time during continuous driving of the OFETs comprising i) a terpolymer dielectric layer with a DPPTTT/PAMS blend semiconductor layer, ii) a PAMS capped dielectric layer with a DPPTTT semiconductor layer, iii) a PMMA capped dielectric layer with a DPPTTT semiconductor layer, and iv) a PMMA capped dielectric layer with a DPPTTT semiconductor layer comprising the sensitising additive of Example 3.

These results show that significant improvements in bias stress resistance are provided by using a capping layer of PAMS or PMMA on the dielectric layer, and a further improvement may be achieved by adding the sensitising additive to the semiconductor layer.

Figure 2(b) shows the change in I_{DS} at different time points during continuous driving of the OFETs comprising (v) a PMMA capped dielectric layer with a DPPPTTT semiconductor layer, (vi) a PMMA capped dielectric layer with a DPPPTTT/PAMS blend semiconductor layer, and (vii) a PMMA capped dielectric layer with a DPPPTTT/PMMA blend semiconductor layer.

- 5 These results show that blending the DPPTTT semiconducting polymer with PAMS or PMMA may improve the bias stress resistance of the OFETs.

Electrical Characteristics

Electrical characteristics of each of the OFETs (Comparative Examples 0-1 and Examples 1-6), in the form of transfer and output curves, were measured to provide field-effect figure-of-merits, ON current (I_{DS}), field-effect mobility (μ) and threshold voltage (V_{th}). These values are shown in Table 2. The transfer curves indicated that the devices are normally-off with negative threshold voltages and the on/off ratio of source-drain current is approximately 10^3 . The highest ON current (I_{DS}) was obtained with the OFETs of Examples 1 (CuTPP), 5 (Pc1) and 6 (Pc2). The charge mobility in the saturation region (μ_{sat}) can be estimated using the equation

15 below:

$$\mu_{sat} = \frac{2L}{WC} \left(\frac{\partial \sqrt{I_D}}{\partial V_G} \right)^2$$

where L is channel length, W is width, C is capacitance, I_D is source-drain current and V_G is the gate-source voltage.

20 **Table 2 - field-effect figure-of-merits of Comparative Examples 0 and 1 and Examples 1-6**

Example	(cm^2/Vs)	V_{th} (V)	SS (mV/dec)	ON/OFF
CE 0*	0.7	-0.6	250	3.7×10^3
CE 1*	0.3	-1.0	200	3×10^3
1	0.3	-1.2	200	3×10^3
2	0.06	-1.2	300	4×10^3
3	0.2	-1.2	450	2.3×10^2
4	0.6	-0.7	260	3.2×10^3
5	0.4	-0.9	370	2.8×10^2

6	0.3	-1	310	2.6×10^2
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*Comparative Examples comprising no sensitising additives.

The output curves show linear and saturation regions and the ohmic contact between the semiconductor and gold electrodes is evident. This indicates that the devices have good charge injection as well as charge transport.

Analyte Sensing

An electronic board with the OFETs suitably mounted upon and electrically connected was used to measure data (I_{DS} , V_{th} , μ) on OFET sensors simultaneously. The board allows V_{DS} and V_{GS} scans over user defined ranges for each individual OFET sensor, which can be used to detect specific target gases (analytes). In order to test the OFETs for sensitivity to different target gases, outlets from cylinders comprising 90 ppm of selected gases, such as NO_2 , CO and SO_2 , were arranged to flow the gases over the OFET sensors, suitably diluted with compressed air to achieve a desired concentration of the target gases. The lowest concentration used was 20 ppb and the highest was 90 ppm. The Comparative and Example OFETs 1-6 were tested by flowing a known concentration of the target gas over the OFET and recording the current. The flow of gas was then switched to only compressed air for a wash-out period and then another flow of a different concentration of target gas was flowed over the OFETs and the current recorded. This was repeated with increasing concentrations of the target gases as shown in the Figures and as discussed below. The %responses of the OFETs to the target gases were calculated using the following equation:

$$\%response = \left(\frac{I_{D,initial} - I_{D,analyte}}{I_{D,initial}} \right) \times 100$$

Figure 3 shows the response (%) of (a) Comparative Example 1 (DPP/PMMA without additives), (b) Example 1 (DPP/PMMA:CuTPP) and (c) Example 2 (DPP/PMMA:ZnPc) OFETs to NO_2 and (d) shows a comparison of the Example 1 and 2 OFET's responses to NO_2 . These results show that the addition of phthalocyanine or porphyrin to DPPTTT solution significantly increased affinity of the DPPTTT/PMMA semiconducting layer to NO_2 target gas.

Out of the different ratios of added phthalocyanine or porphyrin tested, the 100:1 ratio in weight (100 parts being the DPPTTT content) of Examples 1 and 2 gave the highest sensitivities to concentrations down to 50 ppb.

Example 2 OFET was also tested against CO_2 gas, giving a minimum concentration detected of 90 ppm. The results are shown in Figure 4. In comparison, Example 2 OFET shows higher

sensitivity to CO and is less sensitive to CO₂, providing a clear distinction between the two target gases (Figure 4(b)). The responses of Example 2 OFET to CO and NO₂ is comparable.

To investigate discrimination in detection of NO₂ and SO₂, Example 1 OFET was tested with NO₂. As shown in Figure 5(a), Example 2 OFET shows a change in I_{DS} upon exposure to SO₂, with the lowest concentration detected being 4.5 ppm. However, response % decreases for exposures above 13.5 ppm. In comparison, a higher response % is recorded upon exposure of Example 1 OFET to NO₂ compared to SO₂, particularly at concentrations above 13.5 ppm (Figure 5(b)).

Since ZnPc (used in Example 2) is not completely soluble, we identified a readily soluble zinc phthalocyanine, Zinc 2,9,16,23-tetra-tert-butyl-29H,31H-phthalocyanine (TTB-ZnPc) for use in Example 3 OFET. Responses of Example 3 OFET were evaluated upon exposure to NO₂ and CO and the results are shown in Figure 7.

Figure 6 shows the responses of (a) Example 2, (b) Example 3a DPP/PMMA:TTB-ZnPc (100:4 ratio in weight) and (c) Example 3 (100:1 ratio in weight) OFETs to NO₂ exposure and (d) shows a comparison of Example 2 and Example 3 OFETs responses to NO₂.

In comparison with Comparative Example 1, Example 1 and Example 2 OFETs, significantly improved responses are obtained with Example 3 OFET at very low concentrations (<100 ppb) of NO₂ and CO (Figure 7). Example 3 OFET shows a change in I_{DS} (>1%) on exposure to NO₂ at concentrations down to 100s of ppb (Figure 6 (b)). Comparing Figure 6 (b) and (c), Examples 3a and 3 OFET shows improved sensitivity to NO₂ at lower concentrations by reducing the content of added TTB-ZnPc to DPP/PMMA from 100:4 to 100:1. Overall, as depicted in Figure 6(d), higher concentrations of NO₂ (ppms), Example 3 OFET shows twice the change in I_{DS} upon exposure to NO₂ compared to Example 2 OFET.

Example 4 OFET comprising DPP/PMMA with iron phthalocyanine (FePc) was tested against the target gases. FePc is not readily soluble in DCB, but fairly homogenous solutions (post-filtering) were obtained at very low concentrations (0.1 wt%). Figure 8 shows Example 4 OFET's response to (a) NO₂ and (b) CO. As shown in Figure 8, in comparison with Example 3 OFETs, Example 4 OFET shows significantly higher sensitivity to both NO₂ (2.1%) and CO (3.6%) at the lowest detected concentration of 50 ppb. Nonetheless, as expected, Example 4 OFET has higher affinity to CO and hence good discrimination between NO₂ and CO can be provided. Furthermore, more consistent responses with low variation in I_{DS} is observed for Example 4 OFET.

Sensing experiments were also carried out on Example 5 and 6 OFETs comprising DPP/PMMA blends with two different metal-free phthalocyanines (Pc1 and Pc2). The responses upon exposure to NO₂ and CO of these OFETs are shown in Figure 9 (a) and (b) respectively. The uppermost two lines at the peaks in these graphs are the results with the

Example 5 OFET (Pc1) and the lower two lines at the peaks are the results with Example 6 OFET (Pc2). Due to a lack of a chelated metal atom, these additives appear to have less affinity to the gas molecules and therefore a lower sensitivity to NO₂ and CO was observed. However, Example 5 OFET using Pc1 as sensitizer showed higher sensitivity to NO₂ than Example 6 OFET with Pc2. Nonetheless, a higher change (%) in I_{DS} was recorded upon exposure to NO₂ than CO, with lowest detected concentration being 100 ppb.

These results show that the air stable unencapsulated OFETs of the present invention may provide high sensitivities and selectivity in the detection of certain target gases in air flows and therefore may have useful application in the monitoring of said potentially toxic gases. In particular, the OFETs of the present invention may achieve said high sensitivity and selectivity whilst being stable to long term use in air, unlike prior art OFETs which may degrade on use in air. Therefore the OFETs of the present invention may be particularly suitable for gas monitoring in devices intended to be continuously exposed to air (or other atmospheres of oxidising gases), such as in domestic or environmental gas sensors.

15 *Discrimination between NO₂ and CO*

To investigate the possibility of discriminating between NO₂ and CO target gases using the semiconducting materials / OFETs of the present invention, the results of the tests of Examples 3 (labelled DPP:TTB-ZnPc in the figures), 4 (labelled DPP:FePc in the figures), 5 (labelled DPP:PC1 in the figures) and 6 (labelled DPP:PC2 in the figures) with NO₂ and CO target gases at different concentrations were compared in Figures 10a and b. The results show that the all four examples respond significantly to NO₂ and that only Examples 5 (DPPTTT:PMMA - pc1) and Example 6 (DPPTTT:PMMA:pc2, labelled DPP:PC2 in the figures) respond significantly to CO. Therefore these example materials could be used in an array of OFET gas sensors, with each sensor containing a different additive, to discriminate between NO₂ and CO using a combinatorial algorithm to produce a positive determination of the presence of either NO₂ or CO.

Sensitivity to NO₂ in a background of CO

The sensitivity of Examples 4 and 2 to NO₂ was tested in the presence of concentrations of CO of 0.5 ppm, 1.1 ppm and 1.6 ppm using similar testing procedures to those described above. The results are shown in Figures 11a and b (Example 4) and 12a and b (Example 2). Figures 11a and b illustrate that an OFET comprising DPPTTT:PMMA:FePc can quantitatively respond to NO₂ in a fixed background of CO (a) or respond in the same way to NO₂ in varying background levels of CO far in excess of the concentrations of NO₂ being measured. A similar effect is observed for DPPTTT:PMMA:TTB-ZnPc OFETs as shown in Figures 12a and b. This demonstrates the inventions utility in gas sensing applications.

Validation against an independent monitoring station for environmental ambient air monitoring.

Field trials were carried out in Manchester, UK where the developed OFET gas sensors were installed to sample the ambient outdoor air over time using a small pump that provided a flow of air over the sensor array. The recorded data from the sensors were correlated with data from a nearby air quality monitoring station maintained by Manchester City Council and located at GPS coordinates 53.48157, -2.23793, with the OFET devices located at GPS coordinates 53.4741, -2.2350. The sensors and the independent air quality monitoring station are not co-located so this results in a small phase difference, as well as small differences in total gas concentrations measured due to the time taken for air currents to move between different locations as well as local variations in concentration. This does not detract from the results obtained.

As an example, recordings of NO₂ concentration (µg/m³) vs. time and date of data collection measured by three OFET sensors are shown in Figures 13, 14 and 15. Sensor 1 of Figure 13 comprised Example 4 OFET (the DPPTTT:PMMA:FePc semiconducting material), sensor 2 of Figure 14 comprised Example 4 OFET (the DPPTTT:PMMA:FePc semiconducting material) and sensor 3 of Figure 15 comprised Example 3 OFET (the DPPTTT:PMMA:TTP-ZnPc semiconducting material). The sensor responses were low pass filtered to remove spikes (smoothed) and plotted as dotted lines while the output recorded from the air quality monitoring station used as a standard are shown as continuous lines. There is a clear correlation between the NO₂ concentration calculated from the OFET sensors and the live data. For all three sensors, correlating peaks in NO₂ concentration are detected around evening and morning rush hours, which are in correspondence with those reported by live air quality on those specific dates and at those particular locations. Heights of these NO₂ peaks are more significant in the evening rush hours that indicate higher concentrations of NO₂. Moreover, the consistency of patterns of NO₂ concentration obtained from all three sensors shows the reliability of these OFET-based sensors in detecting the gaseous analyte of choice. In addition, the variation in recorded I_{DS} and hence calculated NO₂ concentrations from sensors 1 and 2 (sensitizer FePc) and sensor 3 (sensitizer TTB-ZnPc) is due to different added sensitizers used in the corresponding sensors which demonstrate different sensitivity and selectivity provided by the different sensitizers.

In summary, the present invention provides an organic field effect transistor (OFET) for use in a gas sensor for detecting the presence of one or more target gases, for example CO, CO₂, NO, NO₂, SO₂ or O₃. The OFET comprises a semiconducting layer arranged between a source electrode and a drain electrode, and additionally comprises a dielectric layer and a gate arranged on a substrate. The semiconducting layer is formed of a semiconducting material, suitably a semiconducting polymer, and an additive, suitably a multi-dentate organic ligand, for sensitising the semiconducting material to the presence of said target gases. The sensitising additive is present in the semiconducting material in an amount of up to 10 wt%. The OFET is

suitably unencapsulated and suitably provides a sensitive and selective gas sensor which is stable to continuous operation in air. A gas sensor comprising the OFET and a method of preparing the OFET are also provided.

5 Although a few preferred embodiments have been shown and described, it will be appreciated by those skilled in the art that various changes and modifications might be made without departing from the scope of the invention, as defined in the appended claims.

Throughout this specification, the term “comprising” or “comprises” means including the component(s) specified but not to the exclusion of the presence of other components. The term “consisting essentially of” or “consists essentially of” means including the components
10 specified but excluding other components except for materials present as impurities, unavoidable materials present as a result of processes used to provide the components, and components added for a purpose other than achieving the technical effect of the invention. Typically, when referring to compositions, a composition consisting essentially of a set of components will comprise less than 5% by weight, typically less than 3% by weight, more
15 typically less than 1% by weight of non-specified components.

The term “consisting of” or “consists of” means including the components specified but excluding addition of other components.

Whenever appropriate, depending upon the context, the use of the term “comprises” or “comprising” may also be taken to encompass or include the meaning “consists essentially of”
20 or “consisting essentially of”, and may also be taken to include the meaning “consists of” or “consisting of”.

For the avoidance of doubt, wherein amounts of components in a composition are described in wt%, this means the weight percentage of the specified component in relation to the whole composition referred to. For example, “wherein the semiconducting layer comprises 10 wt% of
25 the sensitising additive” means that 10 wt% of the semiconducting layer is provided by sensitising additive.

The optional features set out herein may be used either individually or in combination with each other where appropriate and particularly in the combinations as set out in the accompanying claims. The optional features for each aspect or exemplary embodiment of the
30 invention as set out herein are also to be read as applicable to any other aspect or exemplary embodiments of the invention, where appropriate. In other words, the skilled person reading this specification should consider the optional features for each exemplary embodiment of the invention as interchangeable and combinable between different exemplary embodiments.

Attention is directed to all papers and documents which are filed concurrently with or previous
35 to this specification in connection with this application and which are open to public inspection

with this specification, and the contents of all such papers and documents are incorporated herein by reference.

5 All of the features disclosed in this specification (including any accompanying claims, and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

10 Each feature disclosed in this specification (including any accompanying claims, and drawings) may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

Claims

1. An organic field effect transistor comprising a semiconducting layer arranged between a source electrode and a drain electrode; wherein the semiconducting layer comprises a semiconducting material and a sensitising additive; and wherein the sensitising additive is present in the semiconducting material in an amount of up to 10 wt%.
5
2. The organic field effect transistor according to claim 1, wherein the sensitising additive comprises a porphyrin or a phthalocyanine.
3. The organic field effect transistor according to claim 1 or claim 2, wherein the sensitising additive comprises a metal.
- 10 4. The organic field effect transistor according to claim 3, wherein the metal is selected from one or more of chromium, manganese, iron, cobalt, nickel, copper, zinc, silver and cadmium.
5. The organic field effect transistor according to any preceding claim, stable to operation in air.
6. The organic field effect transistor according to any preceding claim, wherein the
15 semiconducting material is a semiconducting polymer.
7. The organic field effect transistor according to any preceding claim, wherein the semiconducting material comprises from 60 to 80 wt% of DPPTT and from 20 to 40 wt% PMMA.
8. A semiconducting film composition comprising a semiconducting material and a sensitising
20 additive; wherein the sensitising additive is present in the semiconducting material in an amount of up to 10 wt%.
9. A gas sensor comprising an organic field effect transistor according to any of claims 1 to 7.
10. The gas sensor according to claim 9, wherein the semiconducting layer is sensitive to CO, CO₂, NO, NO₂, SO₂ or O₃.
- 25 11 The gas sensor according to claim 9 or claim 10, which is operable to detect CO, CO₂, NO, NO₂, SO₂ or O₃ in a gaseous mixture at a concentration of 50 parts per billion (ppb).
12. A method of preparing an organic field effect transistor, the method comprising the steps of:
 - a) depositing a gate electrode onto a substrate;
 - 30 b) depositing a dielectric layer onto the gate electrode;

- c) depositing a capping layer onto the dielectric layer;
- d) depositing source and drain electrodes onto the dielectric layer; and
- e) depositing a semiconducting layer onto the source and drain electrodes;

5 wherein the semiconducting layer comprises a semiconducting material and a sensitising additive, wherein the sensitising additive is present in the semiconducting material in an amount of up to 10 wt%.

13. The method according to claim 12, wherein the substrate is a flexible polymeric material, suitably polyethylene naphthalate (PEN).

10 14. The method according to any one of claims 12 to 13, wherein the organic field effect transistor produced by the method is according to any of claims 1 to 7.

15. Use of a multi-dentate organic ligand to improve the sensitivity of a semiconducting material in an organic field effect transistor.

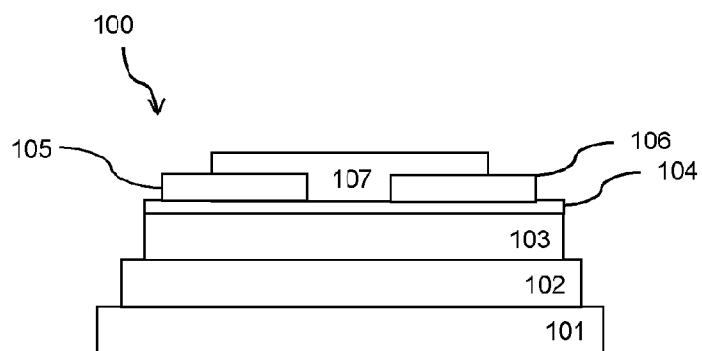
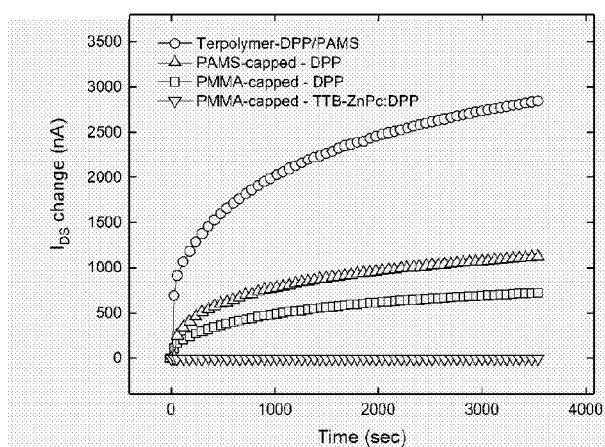
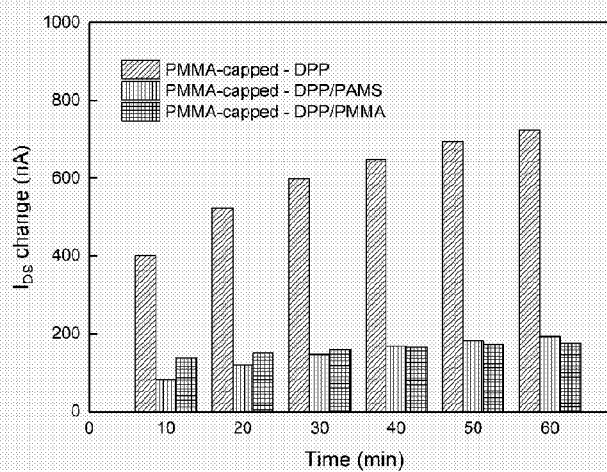


Fig. 1



(a)



(b)

Fig. 2

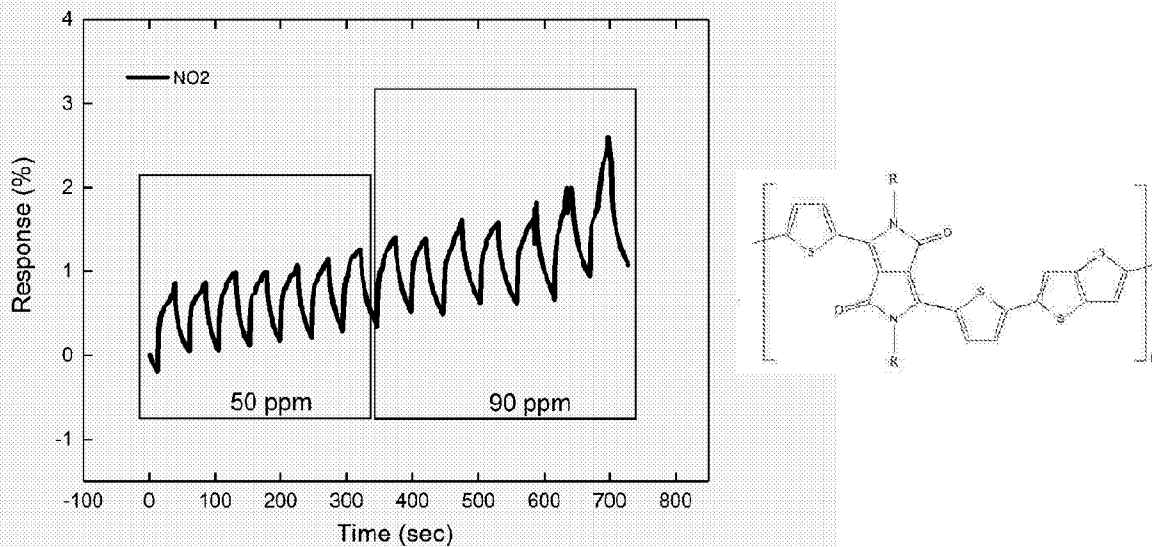


Fig. 3(a)

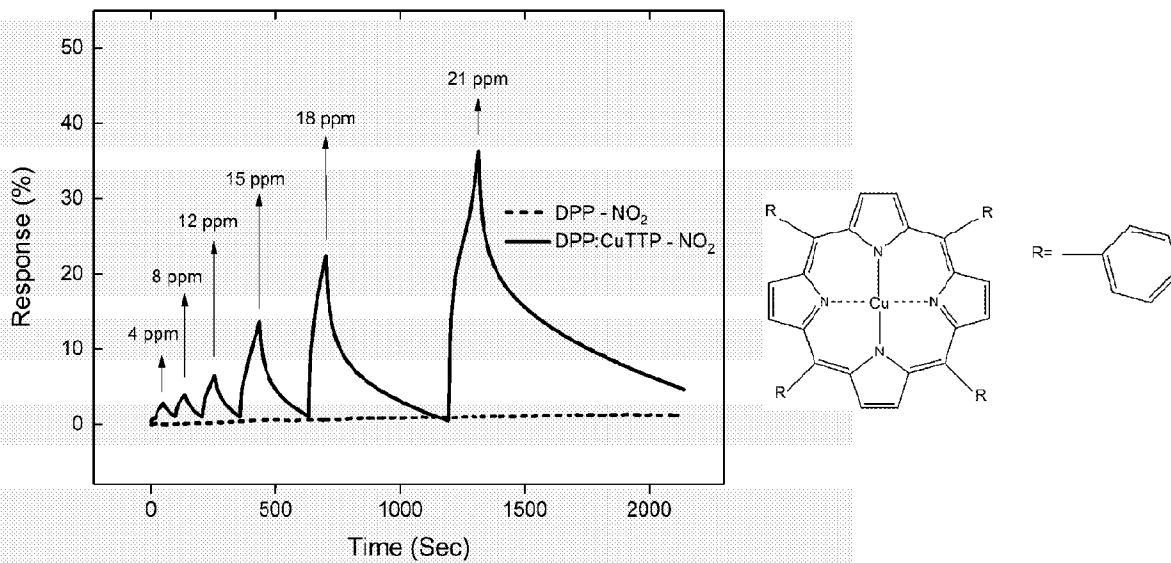


Fig. 3(b)

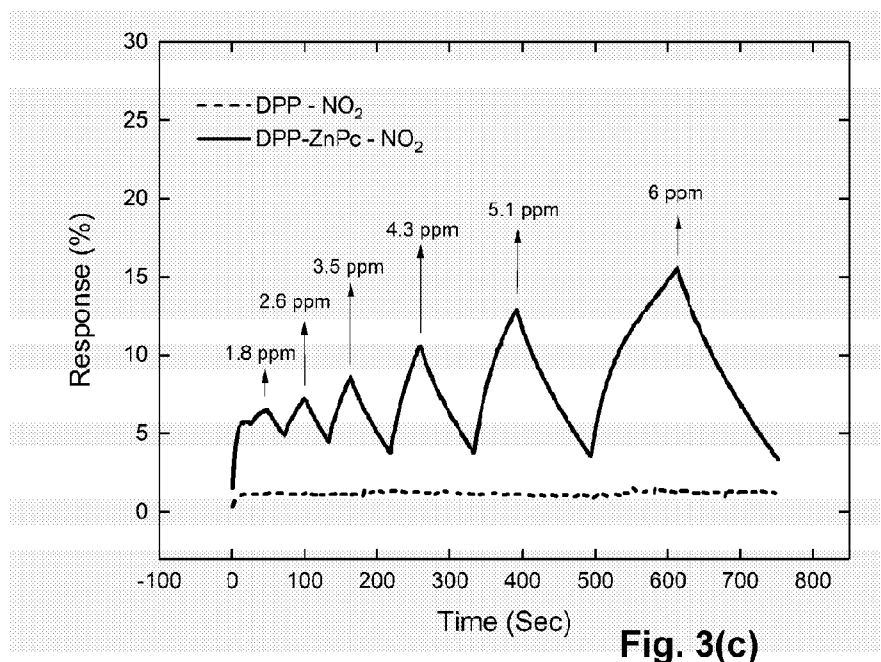


Fig. 3(c)

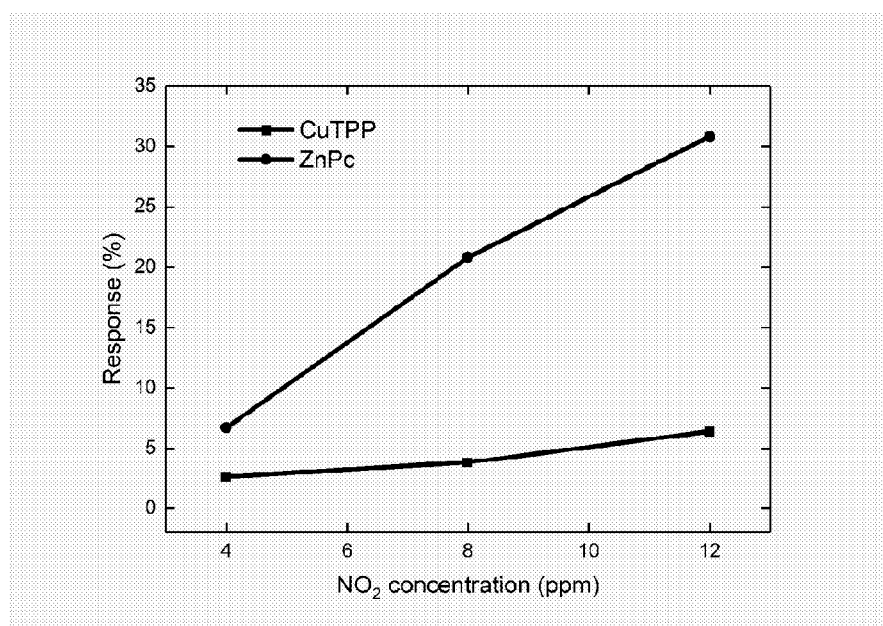


Fig. 3(d)

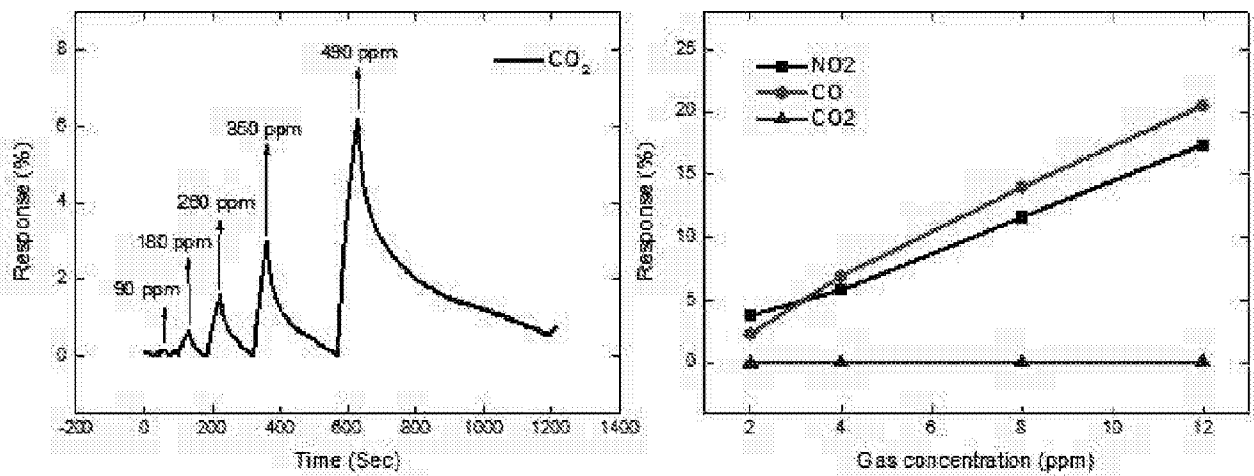


Fig. 4

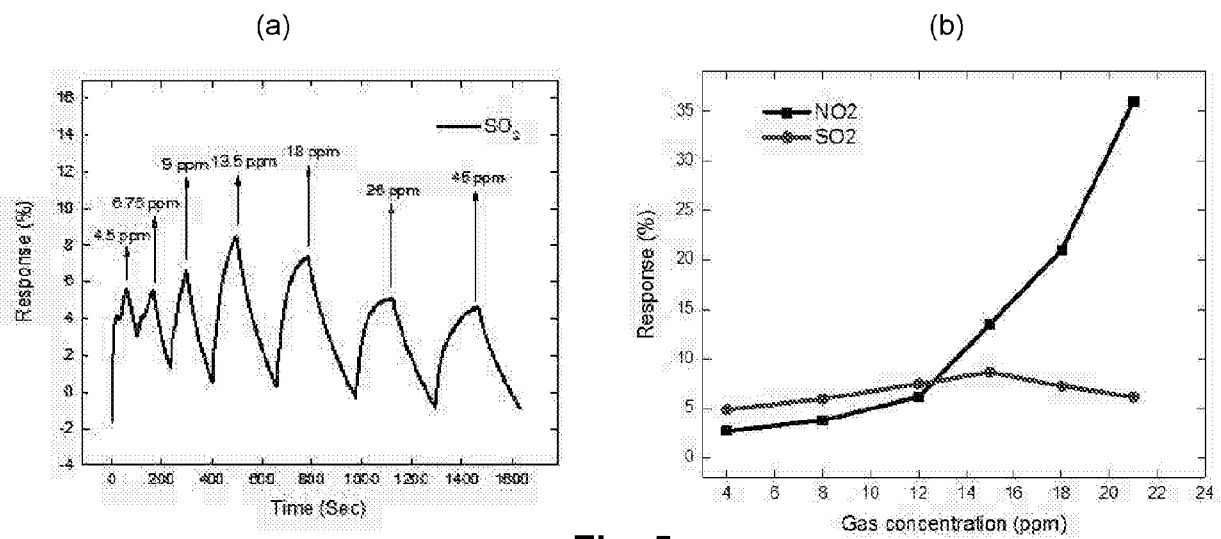


Fig. 5

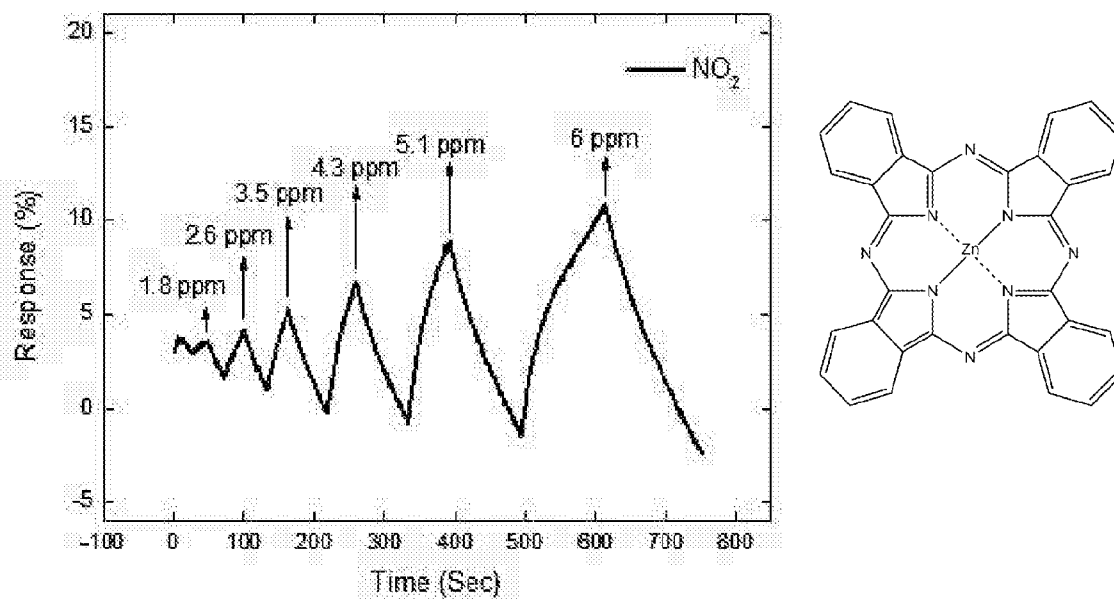


Fig. 6(a)

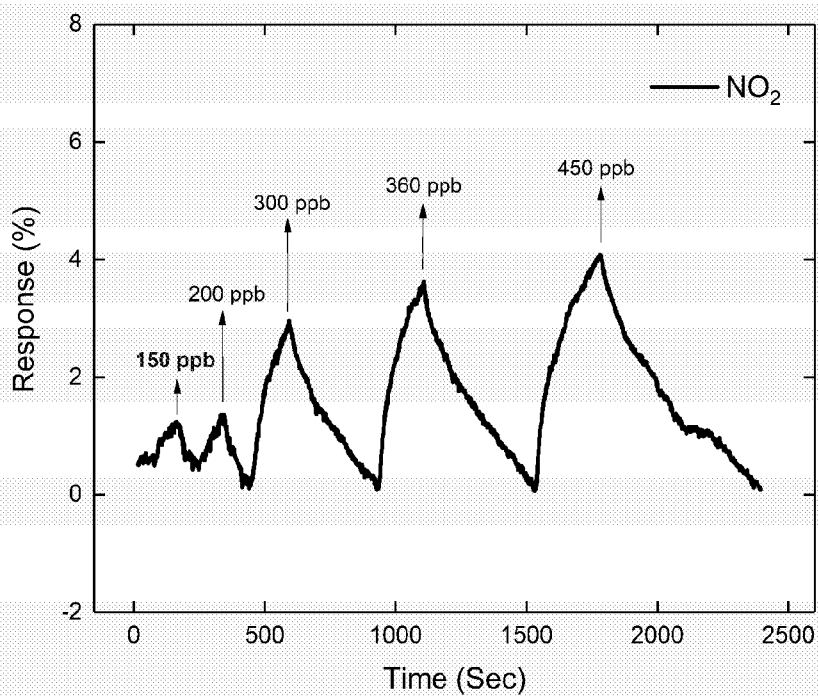


Fig. 6(b)

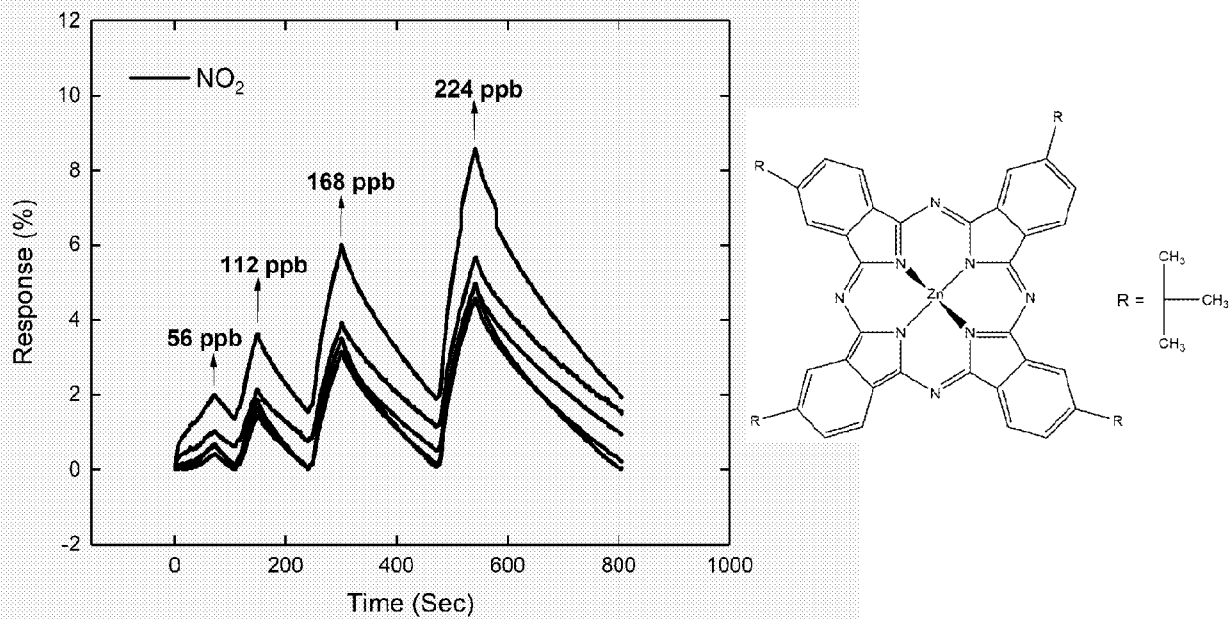


Fig. 6(c)

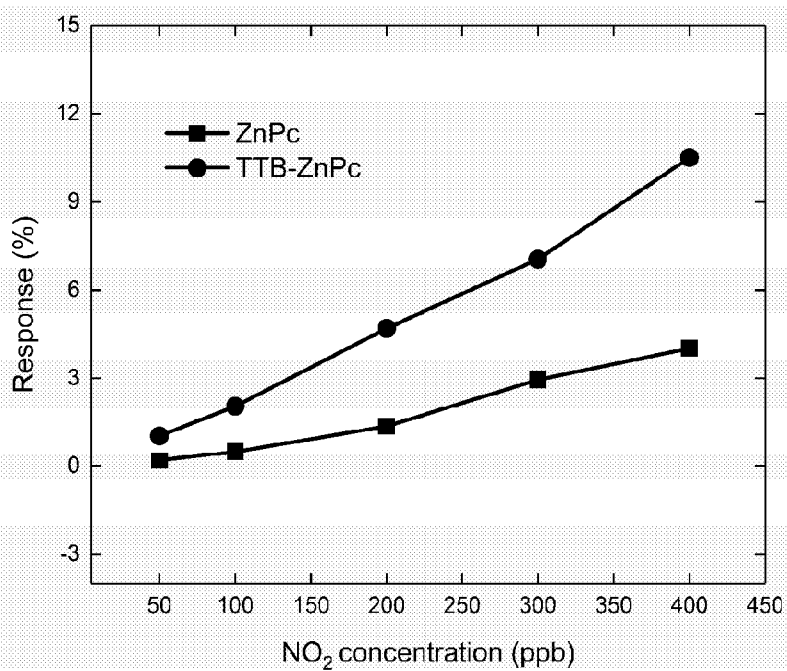


Fig. 6(d)

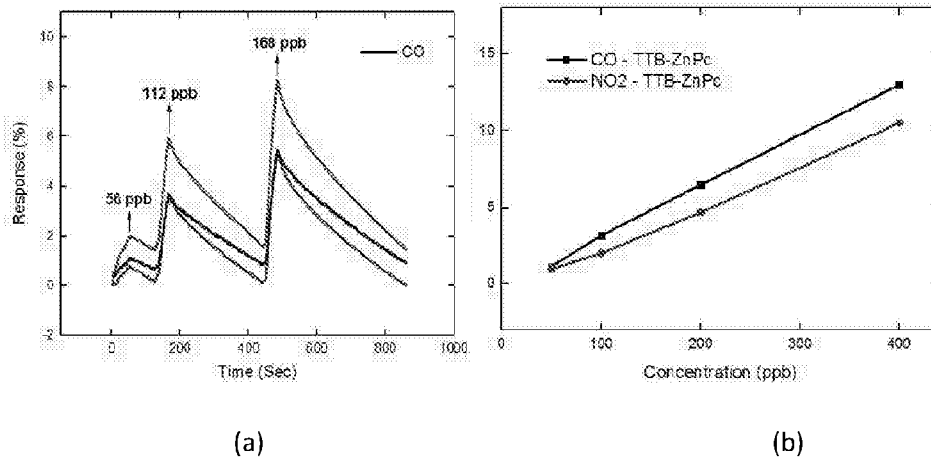


Fig. 7

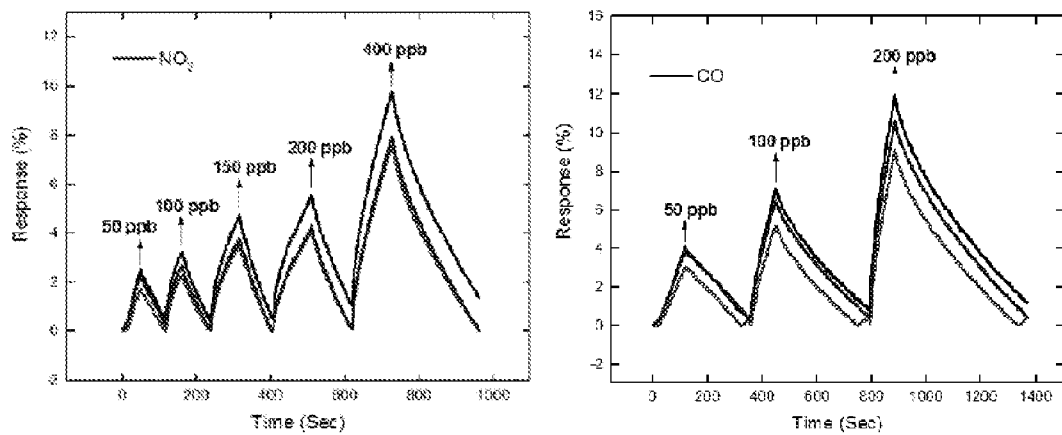


Fig. 8

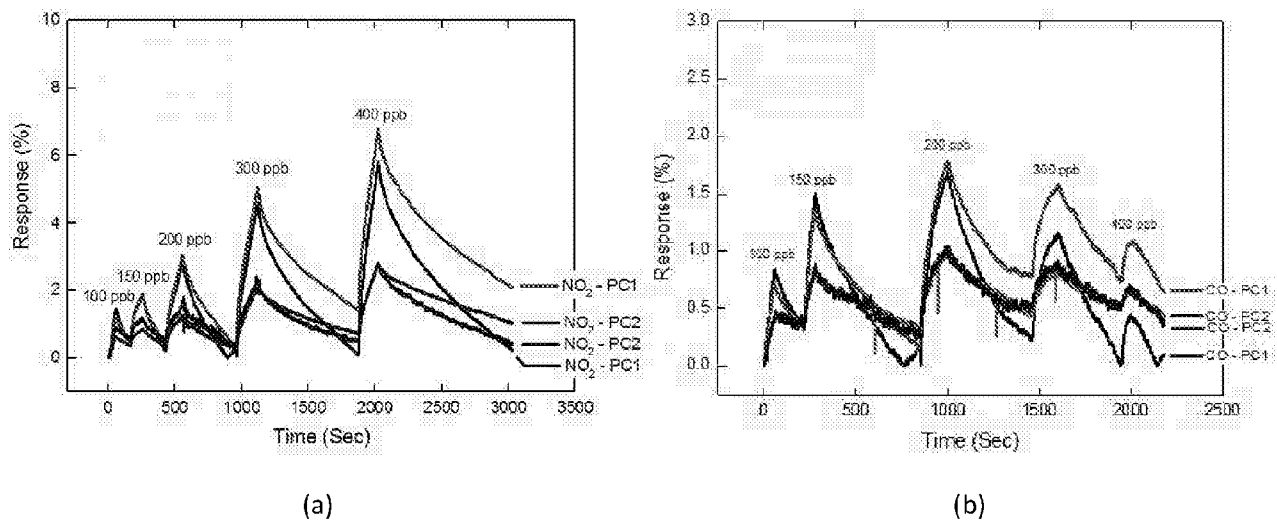


Fig. 9

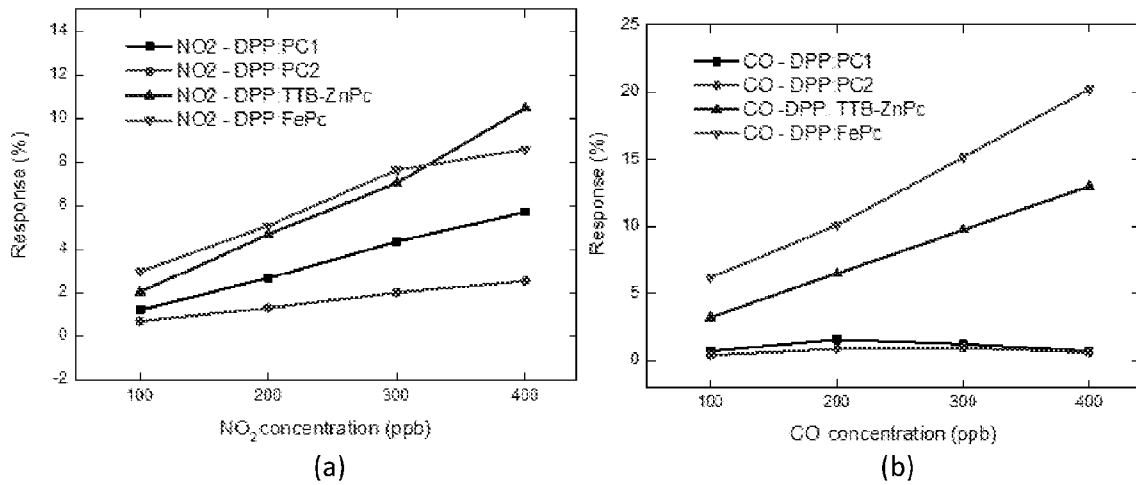


Fig. 10

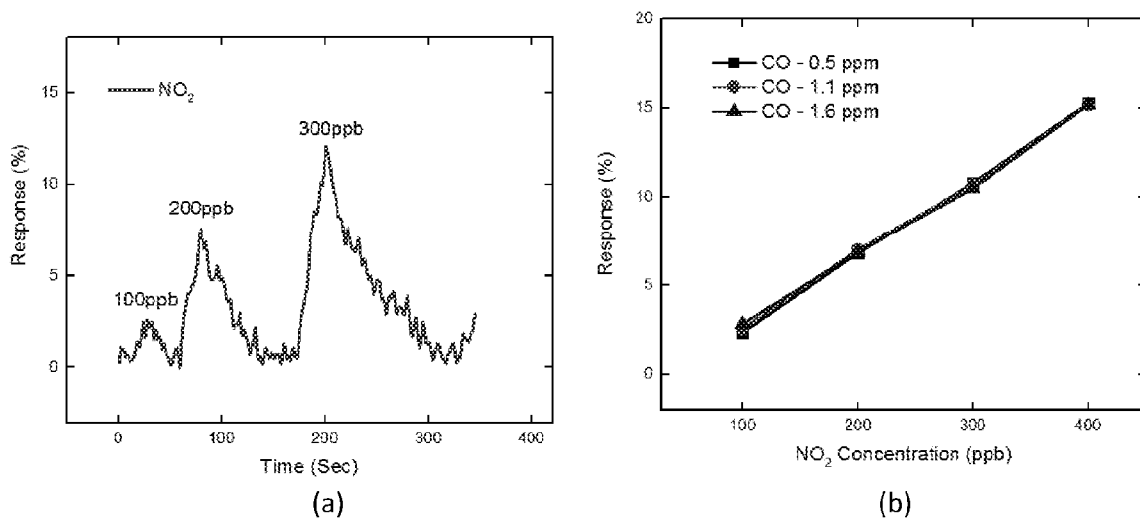


Fig. 11

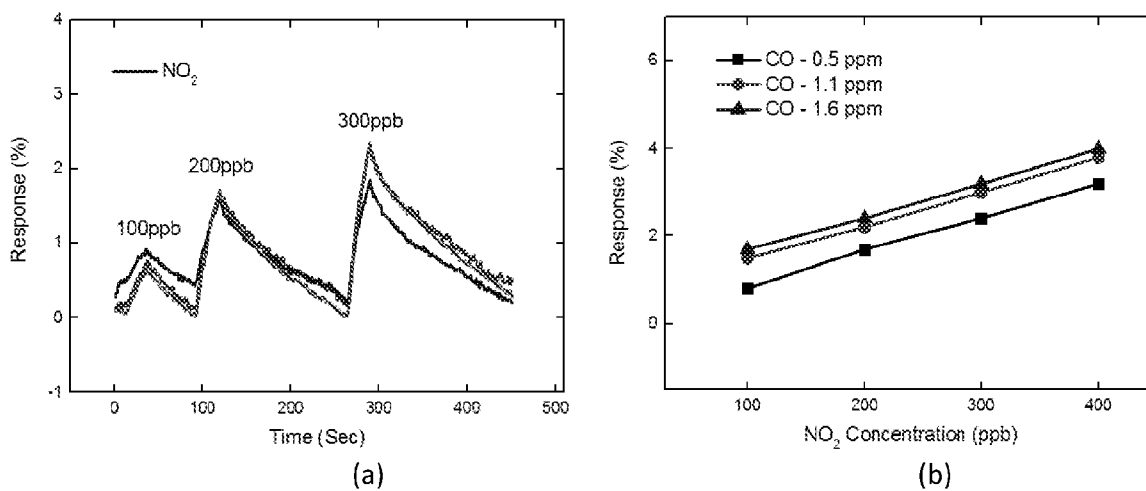
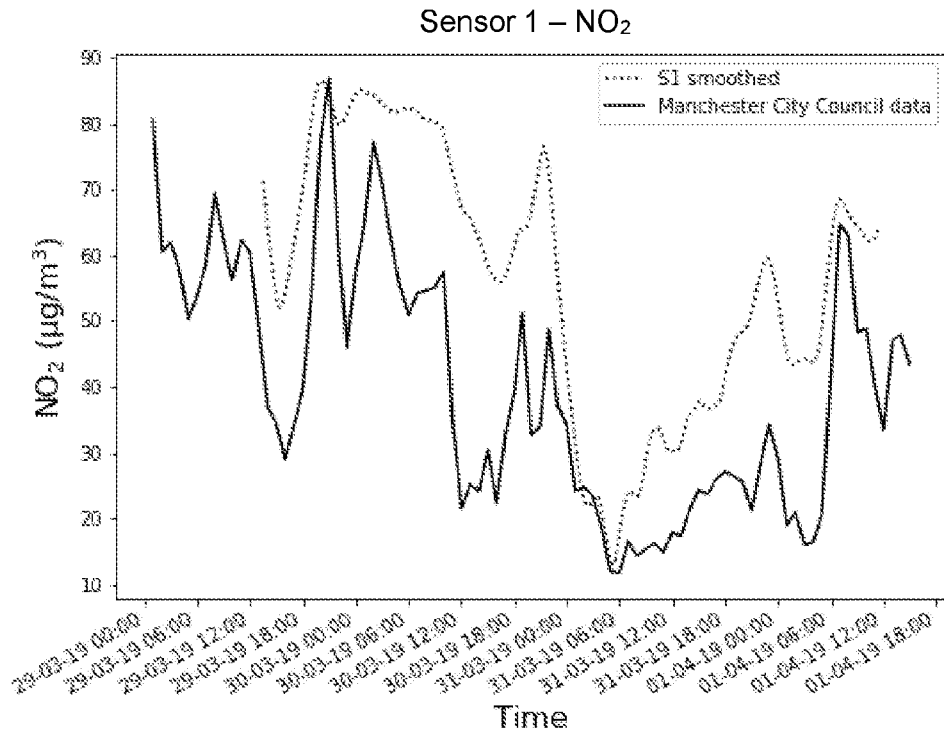
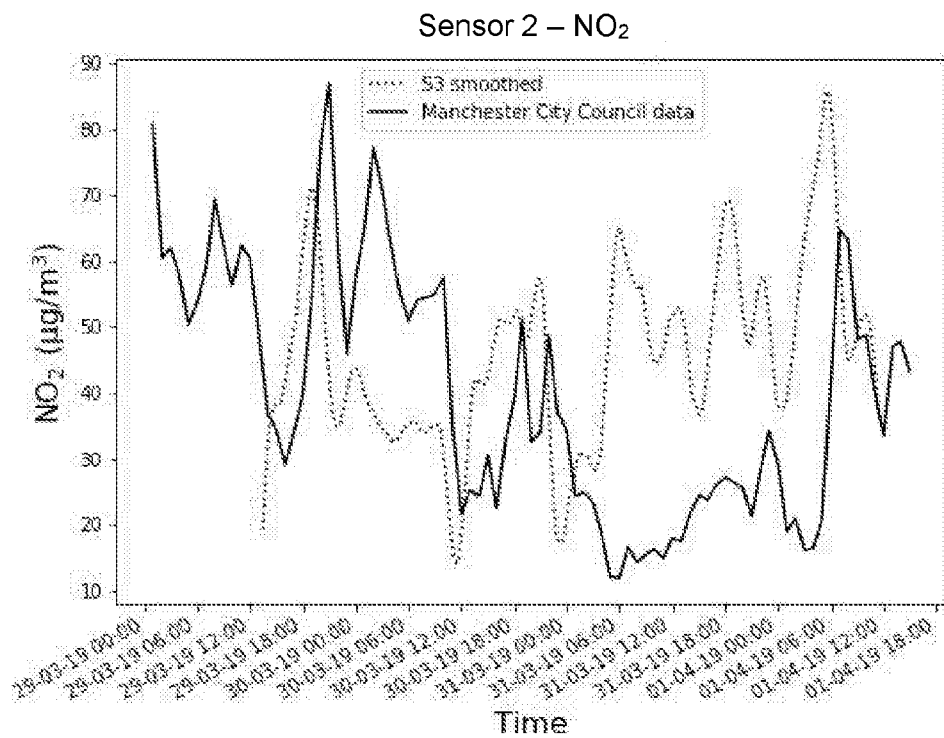
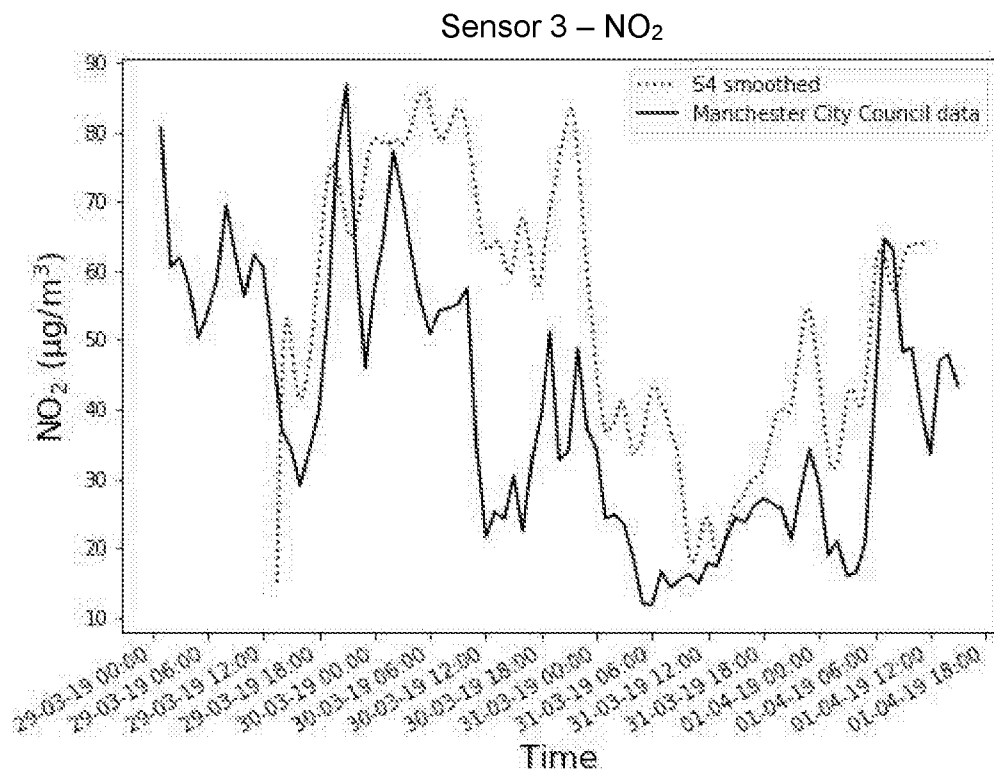


Fig. 12

**Fig. 13****Fig. 14**

**Fig. 15**

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2020/050117

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N27/414 H01L51/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G01N H01L

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2017/338415 A1 (FORD MICHAEL J [US] ET AL) 23 November 2017 (2017-11-23)	1-6,8-15
Y	abstract figures 13,14 paragraphs [0020] - [0024], [0066], [0072], [0080], [0142] - [0159], [0197]	7
X	EP 2 790 238 A1 (NOVALED GMBH [DE]; TECH UNIVERSITÄT DRESDEN [DE]) 15 October 2014 (2014-10-15) abstract figures paragraphs [0032] - [0038], [0043] - [0045] ----- -/--	1,8

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

☒ See patent family annex.

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Date of the actual completion of the international search

26 March 2020

Date of mailing of the international search report

06/04/2020

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Authorized officer

Ruchaud, Nicolas

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2020/050117

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/148812 A1 (WU YILIANG [CA] ET AL) 28 June 2007 (2007-06-28) abstract figures paragraphs [0002], [0023], [0030], [0031], [0052] -----	1,3,4,6, 8
Y	TATE DANIEL J ET AL: "Fully solution processed low voltage OFET platform for vapour sensing applications", 2017 ISOCs/IEEE INTERNATIONAL SYMPOSIUM ON OLFACTION AND ELECTRONIC NOSE (ISOEN), IEEE, 28 May 2017 (2017-05-28), pages 1-3, XP033114251, DOI: 10.1109/ISOEN.2017.7968929 [retrieved on 2017-07-05] abstract figure 1b page 2, lines 21-22 -----	7
A	SUBBARAO NIMMAKAYALA V V ET AL: "Organic field-effect transistors as high performance humidity sensors with rapid response, recovery time and remarkable ambient stability", ORGANIC ELECTRONICS, ELSEVIER, AMSTERDAM, NL, vol. 32, 2 March 2016 (2016-03-02), pages 169-178, XP029474797, ISSN: 1566-1199, DOI: 10.1016/J.ORGEL.2016.02.017 the whole document -----	1-15
A	WO 2017/064243 A1 (BASF SE [DE]) 20 April 2017 (2017-04-20) the whole document -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2020/050117

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2017338415	A1	23-11-2017	NONE
EP 2790238	A1	15-10-2014	EP 2790238 A1 15-10-2014
		US 2014306202	A1 16-10-2014
US 2007148812	A1	28-06-2007	NONE
WO 2017064243	A1	20-04-2017	NONE