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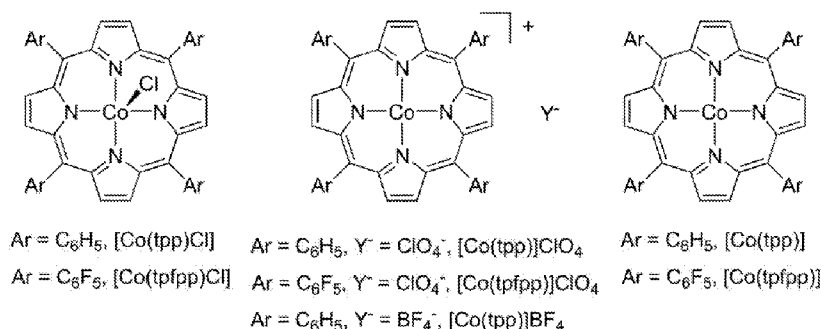
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(54) Title: DETECTION OF AMINES

**FIG. 1**

(57) **Abstract:** A sensor can include a conductive region in electrical communication with at least two electrodes, the conductive region can include a complex, and the complex can include a carbon nanotube that is functionalized by a porphyrin.

DETECTION OF AMINES

CLAIM OF PRIORITY

5 This application claims the benefit of prior U.S. Provisional Application No. 62/142,435 filed on April 2, 2015, which is incorporated by reference in its entirety.

TECHNICAL FIELD

10 The invention features a detector of amines.

FEDERAL SPONSORSHIP

This invention was made with government support under Grant No. DMR-1410718 awarded by the National Science Foundation and under Contract No. W911NF-13-D-0001 awarded by the Army Research Office. The government has certain rights in the invention.

BACKGROUND

15 A detector for meat spoilage can prevent the consumption of unsafe meat or unnecessary discard. One marker of meat decomposition is formation of biogenic amines. Methods for monitoring meat spoilage, such as chromatography, spectrometry, electrophoresis, colorimetry, mass balance, chemiluminescence, and electrochemistry, suffer from one or more drawbacks.

SUMMARY

25 In one embodiment, a sensor can include a conductive region in electrical communication with at least two electrodes, the conductive region including a complex, wherein the complex can include a carbon nanotube that is functionalized by a porphyrin.

In certain embodiments, the porphyrin can include a cobalt porphyrin. The cobalt porphyrin can include a Co^{3+} . The cobalt porphyrin can include a Co^{2+} .

30 In certain embodiments, the carbon nanotube can be non-covalently functionalized by the porphyrin. In certain embodiments, the carbon nanotube can be covalently functionalized by a porphyrin. These covalent functionalization can be accomplished through a diversity of reactions to create new chemical bonds between the porphyrin and the carbon nanotube and include but are

not limited to 1,3-dipolar cycloadditions, reaction with a diazonium ion, coupling reactions to produce an amide linkage, nucleophilic substitution reactions, carbene additions, and nitrene additions.

In certain embodiments, the complex can include a cobalt *meso*-arylporphyrin complex. In certain embodiments, the complex can include a *meso*-tetrakis(pentafluorophenyl)porphyrinato. In certain embodiments, the complex can include a *meso*-tetraphenylporphyrinato. In certain embodiments, the complex can include a *meso*-arylporphyrin.

In certain embodiments, the porphyrin can include a ClO_4^- . In certain embodiments, the porphyrin can include a BF_4^- . In certain embodiments, the porphyrin can include a Cl^- . In certain embodiments, the carbon nanotube can be a single-walled carbon nanotube.

In another embodiment, a method of sensing an analyte can include exposing a sensor to a sample and measuring an electrical property at the electrodes. The sensor can include a conductive region in electrical communication with at least two electrodes, the conductive region including a complex, wherein the complex includes a carbon nanotube that is functionalized by a porphyrin.

In certain embodiment, the method can include detecting an amine. In certain embodiment, the method can include detecting a putrescine. In certain embodiment, the method can include detecting a cadaverine.

In certain embodiment, the detection can be semi-reversible. In certain embodiment, the method can include detecting the analyte below 0.5 ppm. In certain embodiment, the method can include detecting the analyte below 1 ppm. In certain embodiment, the method can include detecting the analyte wirelessly.

In certain embodiment, the method can include detecting the analyte through a wireless radio frequency communication. In certain embodiment, the method can include detecting an output from a radio frequency identification tag including the sensor. In certain embodiment, the method can include detecting nitrogen content.

In certain embodiment, the method can include non-covalently functionalizing the carbon nanotube. In certain embodiment, the method can include covalently functionalizing the carbon nanotube.

In another embodiment, a method of preparing a sensor can include forming a complex including a conductive region in electrical communication with at least two electrodes, the conductive region including a complex, wherein the complex includes a carbon nanotube that is

functionalized by a porphyrin; and placing the conductive material in electrical communication with at least two electrodes.

In another embodiment, a food packaging can include a sensor, wherein the sensor can include a conductive region in electrical communication with at least two electrodes, the
5 conductive region including a complex, wherein the complex can include a carbon nanotube that is functionalized by a porphyrin.

Other aspects, embodiments, and features will be apparent from the following description, the drawings, and the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows structures of cobalt porphyrins employed in detectors. Axial aquo ligands are omitted for clarity.

FIG. 2A shows conductance changes of detectors fabricated from porphyrin-SWCNT composites in response to 30 second exposures of various concentrations of NH_3 in N_2 (quadratic
15 fit); FIG. 2B shows conductance traces of a $[\text{Co}(\text{tpfpp})]\text{ClO}_4$ -SWCNT chemiresistor to three 30 second exposures of various concentrations of NH_3 in N_2 .

FIG. 3 shows responses of detectors fabricated from SWCNT/Co-porphyrin composites to 30 second exposures of 20 ppm NH_3 against reduction potentials (potential of first peak cathodic current as measured by cyclic voltammetry of the compounds in PhCN solution vs. Fc/Fc^+).

FIGS. 4A-4B shows conductance traces of a $[\text{Co}(\text{tpfpp})]\text{ClO}_4$ -SWCNT chemiresistor to three 30 second exposures of 2.5 ppm of a) putrescine (FIG. 4A) and b) cadaverine (FIG. 4B).

FIG. 5 shows responses of $[\text{Co}(\text{tpp})]\text{ClO}_4$ -SWCNT and non-functionalized SWCNT chemiresistors to 30 second exposures of various compounds' vapors (concentration) in N_2 .

FIG. 6A shows conductance trace of $[\text{Co}(\text{tpp})]\text{ClO}_4$ -SWCNT chemiresistor during 30 s
25 exposure to vapors from 1.0 g pork after storage at 22 °C for 4 days; FIG. 6B shows responses of device to 30 second exposures of vapors from various 1.0 g meat samples stored at 22 °C (rt) or 4 °C for 0-4 days.

FIG. 7 shows the detection of meat spoilage.

FIG. 8 shows UV-Vis spectrum of $[\text{Co}(\text{tpfpp})]\text{ClO}_4$ in dichloromethane (DCM) and in
30 methanol (MeOH).

FIG. 9 shows UV-Vis spectrum of $[\text{Co}(\text{tpfpp})\text{Cl}]$ in dichloromethane.

FIG. 10 shows IR spectrum of $[\text{Co}(\text{tpfpp})(\text{H}_2\text{O})_2]\text{ClO}_4$.

FIG. 11 shows IR spectrum of $[\text{Co}(\text{tpfpp})(\text{H}_2\text{O})\text{Cl}]$.

FIG. 12 shows thermal ellipsoid depiction of $[(\text{tpfpp})\text{Co}(\text{ClO}_4)]$. Only the largest components of solvent disorder are shown.

FIG. 13 shows Raman spectrum of $[\text{Co}(\text{tpp})]\text{ClO}_4$ -SWCNT composite (633 nm excitation).

FIG. 14 shows Raman spectrum of tppH_2 -SWCNT composite (633 nm excitation).

FIG. 15 shows Raman spectrum of SWCNTs (633 nm excitation).

FIG. 16A shows average responses of $[\text{Co}(\text{tpp})]\text{ClO}_4$ -SWCNT devices to 1 ppm NH_3 in air relative to those in nitrogen; FIG. 16B shows responses of $[\text{Co}(\text{tpp})]\text{ClO}_4$ -SWCNT devices to 1 ppm NH_3 after 0, 10, and 40 minute exposures to air saturated with water relative to their dry responses; FIG. 16C shows responses of $[\text{Co}(\text{tpp})]\text{ClO}_4$ -SWCNT devices to 1 ppm NH_3 relative to their responses 2 weeks prior.

FIG. 17 shows responses of $[\text{Co}(\text{tpp})]\text{ClO}_4$ -SWCNT and non-functionalized SWCNT chemiresistors to 30 second exposures of various compounds' vapors (concentration) in N_2 .

FIG. 18 shows average responses of three $[\text{Co}(\text{tpp})]\text{ClO}_4$ -SWCNT chemiresistors to three 30 second exposures of vapors from 0.5 g and 1.0 g masses of spoiled pork samples.

FIG. 19 shows an example structure of carbon nanotube functionalization.

DETAILED DESCRIPTION

Chemiresistive detectors for amine vapors can be made from carbon nanotubes by non-covalent modification with cobalt *meso*-arylporphyrin complexes. Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure.

Carbon Nanotubes

Carbon nanotubes can be constructed with length-to-diameter ratio of up to 132,000,000:1, significantly larger than for any other material. These cylindrical carbon molecules have unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology. In particular, owing to their extraordinary thermal conductivity and mechanical and electrical properties, carbon nanotubes find applications as additives to various structural materials.

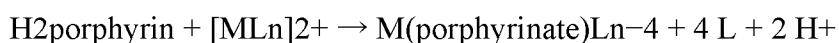
Carbon nanotubes are members of the fullerene structural family. These sheets are rolled at specific and discrete (chiral) angles, and the combination of the rolling angle and radius decides the nanotube properties. For example, whether the individual nanotube shell is a metal or semiconductor. Nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). Individual nanotubes naturally align themselves into "ropes" held together by van der Waals forces, more specifically, pi-stacking.

Applied quantum chemistry, specifically, orbital hybridization best describes chemical bonding in nanotubes. The chemical bonding of nanotubes is composed entirely of sp² bonds, similar to those of graphite. These bonds, which are stronger than the sp³ bonds found in alkanes and diamond, provide nanotubes with their unique strength.

Porphyrin

Porphyrins are a group of heterocyclic macrocycle organic compounds, composed of four modified pyrrole subunits interconnected at their α carbon atoms via methine bridges (=CH-). The parent porphyrin is porphin, and substituted porphines are called porphyrins. The porphyrin ring structure is aromatic, with a total of 26 electrons in the conjugated system. Various analyses indicate that not all atoms of the ring are involved equally in the conjugation or that the molecule's overall nature is substantially based on several smaller conjugated systems.

Porphyrins are the conjugate acids of ligands that bind metals to form complexes. The metal ion usually has a charge of 2+ or 3+. A schematic equation for these syntheses is shown:



where M = metal ion and L = a ligand

A porphyrin without a metal-ion in its cavity is a free base.

Several other heterocycles are related to porphyrins. These include corrins, chlorins, bacteriochlorophylls, and corphins. Chlorins (2,3-dihydroporphyrin) are more reduced, contain more hydrogen than porphyrins, and feature a pyrroline subunit. This structure occurs in a chlorophyll molecule. Replacement of two of the four pyrrolic subunits with pyrrolic subunits results in either a bacteriochlorin (as found in some photosynthetic bacteria) or an isobacteriochlorin, depending on the relative positions of the reduced rings. Some porphyrin derivatives follow Hückel's rule, but most do not.

A benzoporphyrin is a porphyrin with a benzene ring fused to one of the pyrrole units. eg verteporfin is a benzoporphyrin derivative.

Researchers have reported porphyrin-functionalized CNTs bound covalently with an ester linkage, in which CNTs bearing carboxylic groups on the sidewall and at the terminal were esterified with hydroxyl porphyrins. See, e.g, Baskaran D, Mays JW, Zhang XP, Bratcher MS. J. 2005. p. 6916, incorporated by reference herein.

5 Researchers have also reported the synthesis of a novel covalently porphyrin-functionalized single walled carbon nanotube nanohybrid constructed with a unique direct linkage using in situ generated diazonium compounds. See, e.g., Guo Z, Du F, Ren DM, Chen YS, Zheng JY, Liu ZB, Tian JG. J. 2006. p. 3021, incorporated by reference herein.

Generally, there are two disadvantages in porphyrin-functionalized CNTs process, one is
10 the low quantity porphyrin (<20 wt%) grafted to the surface of CNTs, another is that the structure of CNTs was badly destroyed because carboxyl groups on MWNT surface are prepared by strong oxidative acid treatment. There have been few reports on the functionalization of CNTs to overcome these two weaknesses simultaneously. However, when a covalent porphyrin and its complexes (Co²⁺, Zn²⁺) functionalized by MWNTs, they were successfully synthesized by the
15 reaction of the carboxyl on the surface of MWNTs which was synthesized to use carbon radicals generated by the thermal decomposition of azodiisobutyronitrile (AIBN) with 5-p-hydroxyphenyl-10,15,20-triphenyl-porphyrin and its complexes (Co²⁺, Zn²⁺). The quality of porphyrin attached to the MWNTs was determined from thermogravimetric analysis (TGA) of the MWNTs, which showed a weight loss of about 60%.

20 Carbon nanotube (CNT) compositions can be prepared by covalently grafting a Co(II) porphyrin to functionalized multiwalled carbon nanotubes (MWCNTs) via zwitterionic functionalization of the CNT sidewalls followed by a SN₂ substitution reaction. The MWCNT-Co-porphyrin compositions, mixed with Nafion, displayed excellent catalytic performance for oxygen reduction in acidic media (pH range, 0.0–5.0) at room temperature. With
25 low catalyst loading, the oxygen reduction rates achieved are more than 1 order of magnitude higher than previously reported values for similar Co-porphyrin catalysts. These results demonstrate the advantages of systems of MWCNTs covalently linked to electrocatalytic molecules. The electrodes are easily fabricated by a drop-casting vacuum drying procedure. Rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) measurements revealed
30 the mechanism to be a direct four-proton and four-electron reduction of oxygen to water. These results demonstrate that new MWCNT electrocatalytic systems are potential substitutes for

platinum or other metal-based cathode materials in proton conducting membrane fuel cells. This is described, for example in Cobalt Porphyrin Functionalized Carbon Nanotubes for Oxygen Reduction, *Chem. Mater.*, 2009, 21(14), pp. 3234-3241 (June 2009), incorporated by reference herein.

5 Used to Detect Spoilage

Putrescine, or tetramethylenediamine, is a foul-smelling organic chemical compound $\text{NH}_2(\text{CH}_2)_4\text{NH}_2$ (1,4-diaminobutane or butanediamine) that is related to cadaverine; both are produced by the breakdown of amino acids in living and dead organisms and both are toxic in large doses.

10 Cadaverine is a foul-smelling diamine compound produced by protein hydrolysis during putrefaction of animal tissue. Cadaverine is a toxic diamine with the formula $\text{NH}_2(\text{CH}_2)_5\text{NH}_2$, which is similar to putrescine. Cadaverine is also known by the names 1,5-pentanediamine and pentamethylenediamine.

Through changes in the metal's oxidation state, the electron-withdrawing character of the porphyrinato ligand, and the counteranion, the magnitude of chemiresistive response to ammonia
15 can be improved. The devices can exhibit sub-ppm sensitivity and high selectivity toward amines as well as good stability to air, moisture, and time. These chemiresistors can be used in the detection of various biogenic amines (e.g., putrescine, cadaverine) and in the monitoring of spoilage in raw meat samples (e.g., chicken, pork, salmon, cod).

20 Sensor Properties and Applications

Interest in the synthesis and study of porphyrin complexes with variable valence metals results from their potential application as chemical sensors, photo chromic materials, and redox catalysts.

A sensor can include a conductive region in electrical communication with at least two
25 electrodes, the conductive region including a complex, and the complex includes a carbon nanotube that is functionalized by a porphyrin. The functionalization can be covalent or non-covalent. The carbon nanotube can be covalently functionalized by a porphyrin by a bond between a phenyl group pendant to the porphyrin and the carbon nanotube through 1,3-dipolar cycloadditions, reaction with a diazonium ion, coupling reactions to produce an amide linkage,
30 nucleophilic substitution reactions, carbene additions, and nitrene additions. Other types of functionalization can also be used. See, for example, Guo, Z.; Du, F.; Ren, D.; Chen, Y.; Zheng,

J.; Liu, Z.; Tian, J. J. *Mater. Chem.* 2006, 16, 3021; Lipińska, M. E.; Rebelo, S. L. H.; Pereira, M. F. R.; Figueiredo, J. L.; Freire, C. *Mater. Chem. Phys.* 2013, 143, 296–304; Zhang, W.; Shaikh, A. U.; Tsui, E. Y.; Swager, T. M. *Chem. Mater.* 2009, 21, 3234–3241, each of which is incorporated by reference in its entirety. The sensor can behave as a dosimeter giving an irreversible response to one or more nitrogen bases.

For health and economic reasons, there is interest from meat providers and consumers in sensors to monitor its spoilage. See, for example, K.-H. Eom, et al., *Int. J. Distrib. Sens. Networks* 2014, 2014, 1–9, which is incorporated by reference in its entirety. A detector for meat spoilage can prevent the consumption of unsafe meat or unnecessary discard. One marker of meat decomposition is formation of biogenic amines (BAs). Among the BAs in food are putrescine (butane-1,4-diamine) and cadaverine (pentane-1,5-diamine). BAs are formed through microbial enzymatic decarboxylation of amino acids and by amination of carbonyls. See, for example, A. Naila, et al., *J. Food Sci.* 2010, 75, R139–R150; J. Karovičová, et al., *Chem. Pap.* 2005, 59, 70–79, each of which is incorporated by reference in its entirety.

Many methods for monitoring meat spoilage rely on detection of amines, or total volatile basic nitrogen (TVBN). Strategies for the detection of BAs include chromatography, spectrometry, electrophoresis, colorimetry, mass balance, chemiluminescence, and electrochemistry. See, for example, Z. Karpas, et al., *Anal. Chim. Acta* 2002, 463, 155–163; L. V. Jørgensen, et al., *J. Agric. Food Chem.* 2001, 49, 2376–2381; Á. Kovács, et al., *J. Chromatogr. A* 1999, 836, 305–313; H. Li, et al., *Anal. Methods* 2014, 6, 6271–6277; b) T. L. Nelson, et al., *Analyst* 2007, 132, 1024–1030; c) M. S. Maynor, et al., *Org. Lett.* 2007, 9, 3217–3220; C. Di Natale, et al., *Sens. Actuators, B* 1997, 44, 521–526; Y. Yano, et al., *Lebensm.-Wiss. u.-Technol.* 1996, 29, 498–502; M. Wimmerová, et al., *Biosens. Bioelectron.* 1999, 14, 695–702; D. Carelli, et al., *Biosens. Bioelectron.* 2007, 23, 640–647, each of which is incorporated by reference in its entirety. However, these all suffer from one or more drawbacks: extensive sample preparation prior to analysis; expensive, cumbersome instruments with high power consumption; highly trained personnel to operate; and line of sight required to read output.

Electronic sensors such as chemiresistors offer solutions to these drawbacks. They can take measurements in real time with the as-is sample; they can be fabricated cheaply; they can be portable with low power requirements and readily integrated into electronic circuitry without direct visual (line of sight) observation needed to obtain the readout. Carbon nanotubes are

particularly well suited for use in chemiresistors as they are highly sensitive to changes in their electronic environments and do not require high operating temperatures. See, for example, U. Latif, et al., *Sensors* 2011, 11, 8611-8625; D. R. Kauffman, et al., *Angew. Chem.* 2008, 120, 6652-6673; b) D. R. Kauffman, et al., *Angew. Chem. Int. Ed.* 2008, 47, 6550-6570; P. M.

5 Schweizer-Berberich, et al., *Sens. Actuators, B* 1994, 19, 282-290, each of which is incorporated by reference in its entirety.

Although non-functionalized single-walled carbon nanotubes (SWCNTs) can detect amines chemiresistively, their sensitivity and specificity to amines can be improved through functionalization.

10 Functionalization of CNTs

SWCNTs can be functionalized covalently or non-covalently with other molecules in order to impart sensitivity or selectivity for a desired analyte. See, for example, K. A. Mirica, et al., *Angew. Chem.* 2012, 124, 10898-10903; K. A. Mirica, et al., *Angew. Chem. Int. Ed.* 2012, 51, 10740-10745; J. M. Schnorr, et al., *Chem. Mater.* 2011, 23, 646-657, each of which is
15 incorporated by reference in its entirety. In particular, non-covalent functionalization allows for facile functionalization without disruption of the electronic properties of the CNTs that can accompany covalent functionalization. See, for example, W. Maser, et al., in *Functionalized Nanoscale Materials, Devices and Systems* (Eds.: A. Vaseashta, I.N. Mihailescu), Springer, Dordrecht, The Netherlands, 2008, pp. 101-120, which is incorporated by reference in its entirety.

20 Covalent functionalization is based on the formation of a covalent linkage between functional entities and the carbon skeleton of nanotubes. It could also be divided into direct covalent sidewall functionalization and indirect covalent functionalization with carboxylic groups on the surface of CNTs. Direct covalent sidewall functionalization is associated with a change in hybridization from sp² to sp³ and a simultaneous loss of conjugation. Indirect covalent
25 functionalization takes advantage of chemical transformations of carboxylic groups at the open ends and holes in the sidewalls. These carboxylic groups might have existed on the as-grown CNTs and also be further generated during oxidative purification. In order to increase the reactivity of CNTs, the carboxylic acid groups usually need to be converted into acid chloride and then undergo an esterification or amidation reaction. The drawback of covalent functionalization
30 is that the perfect structure of CNTs has to be destroyed, resulting in significant changes in their physical properties.

Non-covalent functionalization is mainly based on supramolecular complexation using various adsorption forces, such as Van der Waals force, hydrogen bonds, electrostatic force and π -stacking interactions. Compared to the chemical functionalization, non-covalent functionalization has the advantages that it could be operated under relatively mild reaction conditions and the perfect graphitic structure of CNTs could be maintained.

Porphyrins are an attractive platform for functionalizing SWCNTs because their aromatic core is capable of non-covalently binding to the walls of the SWCNTs with the π system. See, for example, A. Satake, et al., *Chem. Mater.* **2005**, 716–724; H. Murakami, et al., *Chem. Phys. Lett.* **2003**, 378, 481–485; Q. Zhong, et al., *ACS Nano* **2013**, 7, 3466–3475; H. Li, et al., *J. Am. Chem. Soc.* **2004**, 126, 1014–1015, which is incorporated by reference in its entirety.

To detect amines, SWCNTs can be functionalized with cobalt porphyrins, which can bind to amines, can be tuned rationally, and offer an opportunity to examine the effects of oxidation state in amine sensing as both Co^{2+} and Co^{3+} species are accessible. See, for example, H. Sugimoto, et al., *Bull. Chem. Soc. Jpn.* 1981, 54, 3425–3432, which is incorporated by reference in its entirety. The synthesis and properties of cobalt(II) and cobalt(III) are described, for example, by Chizhova, N.V., et al., *Synthesis and Spectral Properties of Cobalt (II) and Cobalt (III) Tetraarylporphyrinates*, *Russian J. of Inorganic Chemistry*, Vol. 58, No. 6, 2013, pp. 836–840, also incorporated by reference herein.

The sensitivity to amines can benefit from increasing electrophilicity of the Co center by using a relatively electron-withdrawing porphyrin, a weakly coordinating counteranion, and a high oxidation state. A series of Co porphyrins (FIG. 1) can be synthesized for comparison between *meso*-tetraphenylporphyrinato (tpp) and the more electron-withdrawing *meso*-tetrakis(pentafluorophenyl)porphyrinato (tpfpp) ligand, between Cl^- and the more weakly coordinating ClO_4^- and BF_4^- counteranions, and between Co^{3+} and more electron-rich Co^{2+} .

Cobalt(III) porphyrins incorporated in a SWNT network can be active in the chemoresistive detection of an analyte. Sensitivity to an analyte can benefit from increasing the electrophilicity of the cobalt(III) center toward amines through the use of both a relatively electron-withdrawing porphyrin ligand and a weakly coordinating counter anion. Therefore, a series of cobalt(III) porphyrins can allow for comparison between

5,10,15,20-tetraphenylporphyrinato (tpp) and the more electron-withdrawing 5,10,15,20

tetrakis(pentafluorophenyl)porphyrinato (tpfpp) ligand as well as between Cl^- and the more weakly coordinating ClO_4^- counteranion.

5 Porphyrins with a sterically protected metal center may provide enhanced selectivity by excluding compounds that are larger or that would bind to the metal center in an η^1 fashion perpendicular to the approximate plane of the porphyrin ring (e.g., CO, MeCN). A canopied pyrrole can give such protection by restricting the space around a tervalent group 9 metal center when incorporated into a porphyrin ligand's structure, preventing the binding of larger interferent molecules and other coordinating volatile organic compounds while still allowing the particularly small molecule to access the metal center in a flatter, side-on fashion and potentially excluding larger molecules that can be forced to bind end-on due to the canopy's obstruction of space higher above the metal center.

10 A chemiresistive detector for amines can be fabricated from Co porphyrin/SWCNT composites. Tuning the Co oxidation state, ligand, and primary coordination sphere of the complex can lead to improvements in sensitivity toward amines, which are detected rapidly at sub-ppm concentrations and with high selectivity. The devices can be used to monitor meat for spoilage by detecting volatile BAs. The system represents an inexpensive, portable method for following the decomposition of various types of meat.

EXAMPLE

20 The (6,5) chirality-enriched SWNTs (SG65) were purchased from SouthWest NanoTechnologies. Carbon monoxide gas (99.3%) was purchased from Airgas. 5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin (tpfppH_2) was purchased from Frontier Scientific. Perchloric acid (70%) was purchased from Sigma-Aldrich. Aluminum oxide (activated, neutral, Brockmann Grade I, 58 Å) was purchased from Alfa Aesar. Solvents were purchased from Sigma-Aldrich or Avantor Performance Materials (Macron Fine Chemicals or J. T. Baker) and used as received.

UV-Vis spectra were recorded on a Cary 4000 UV-visible spectrophotometer. FT-IR spectroscopy was performed with use of a Thermo Scientific Nicolet 6700 FT-IR spectrometer (ATR mode, Ge). NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer and were referenced to the proton resonances resulting from incomplete deuteration of the NMR solvent (^1H) or to α,α,α -trifluorotoluene added as an internal reference standard (^{19}F).

Cyclic voltammetric measurements were taken using a Biologic VMP3 potentiostat with a scan rate of 100 mV/s under N₂ gas using a Ag/Ag⁺ pseudo-reference electrode, Pt counter electrode, and glassy carbon working electrode in benzonitrile solvent with 0.1 M tetra-*n*-butylammonium hexafluorophosphate supporting electrolyte. Potentials were referenced to Fc/Fc⁺.

Synthetic Procedures

5,10,15,20-Tetraphenylporphyrin (tppH₂), 5,10,15,20-tetraphenylporphyrinatocobalt(II) [Co(tpp)], 5,10,15,20-tetrakis(pentafluorophenyl)porphyrinatocobalt(II) [Co(tpfpp)], chloro(5,10,15,20-tetraphenylporphyrinato)cobalt(III) monohydrate [Co(tpp)Cl(H₂O)], 5,10,15,20-tetraphenylporphyrinatocobalt(III) perchlorate dihydrate [Co(tpp)(H₂O)₂]ClO₄, and 5,10,15,20-tetraphenylporphyrinatocobalt(III) tetrafluoroborate dihydrate [Co(tpp)(H₂O)₂]BF₄ were synthesized according to literature procedures. See, for example, Adler, A. D., et al., J. Org. Chem. 1966, 32, 476; Dorough, G. D., et al., J. Am. Chem. Soc. 1951, 73, 4315–4320; Kadish, K. M., et al., J. Am. Chem. Soc. 1990, 112, 8364–8368; Sakurai, T., et al., Bull. Chem. Soc. Jpn 1976, 49, 3042–3046; Sugimoto, H., et al., Bull. Chem. Soc. Jpn 1981, 54, 3425–3432, which is incorporated by reference in its entirety.

Synthesis of 5,10,15,20-tetrakis(pentafluorophenyl)porphyrinatocobalt(III) perchlorate dihydrate, [Co(tpfpp)(H₂O)₂]ClO₄.

[Co(tpfpp)] (0.060 g, 0.058 mmol) was dissolved in methanol (60 mL). A 10% aqueous HClO₄ solution (2 mL) was added, and air was bubbled through the solution while stirring for 72 h at rt. The reaction mixture was concentrated with use of rotary evaporation. The resulting purple crystals were isolated by vacuum filtration and allowed to dry under air to give the product (0.043 g) in 66% yield. ¹H NMR (400 MHz, CD₃OD): δ 9.65 (s); ¹⁹F NMR (376 MHz, CD₃OD): δ -140.24 (dd, 8F, *J* = 21 and 6.8 Hz), -154.26 (t, 4F, *J* = 21 Hz), -164.14 (td, 8F, *J* = 21 and 6.8 Hz).

Synthesis of chloro(5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato)cobalt(III) monohydrate, [Co(tpfpp)Cl(H₂O)].

[Co(tpfpp)] (0.060 g, 0.058 mmol) was dissolved in methanol (60 mL). Concentrated HCl (0.6 mL) was added, and air was bubbled through the solution while stirring for 72 h at rt. The

reaction mixture was concentrated with use of rotary evaporation. The resulting purple crystals were isolated by vacuum filtration and allowed to dry under air to give the product (0.023 g) in 37% yield. ^1H NMR (400 MHz, CD_3OD): δ 9.65 (s); ^{19}F NMR (376 MHz, CD_3OD): δ -140.23 (dd, 8F, $J = 21$ and 6.8 Hz), -154.24 (t, 4F, $J = 21$ Hz), -164.12 (td, 8F, $J = 21$ and 6.8 Hz).

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Device Preparation

Devices were prepared on microscope glass slides (VWR) cleaned by sonication in acetone. The glass slides were fitted with a custom aluminum mask, and using a thermal evaporator purchased from Angstrom Engineering, a 10 nm layer of chromium (99.99%, R.D. Mathis) was deposited onto the glass, followed by 100 nm of gold (99.99%, R.D. Mathis).

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In a typical device, 0.25 mg (21 μmol C) of SWNTs and 0.44 mmol porphyrin were suspended in 1.0 mL 1,2-dichlorobenzene and sonicated briefly at room temperature. The resulting dispersion was drop-casted using a micropipette onto the glass slide in between the gold electrodes. The solvent was removed in vacuo. The application of the dispersion followed by the removal of the solvent was repeated until the resistance across the SWNT network reached a resistance of 10-100 k Ω as measured by a multimeter.

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Crystallographic Details

Low-temperature diffraction data of $[(\text{tpfpp})\text{Co}(\text{ClO}_4)]$ (ϕ - and ω -scans) were collected on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart APEX2 CCD detector with an I μ S micro-source Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). Absorption and other corrections were applied using SADABS. All structures were solved by direct methods using SHELXS, and refined against F ^{2} on all data by full-matrix least squares with SHELXL-97. See, for example, G. M. Sheldrick, *Acta Cryst.* 2008, A64, 112-122, which is incorporated by reference in its entirety. A summary of crystal and refinement data is shown in table 1.

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The complex $[(\text{tpfpp})\text{Co}(\text{ClO}_4)]$ crystallized in the $\text{P}\bar{1}$ space group with one molecule of $[(\text{tpfpp})\text{Co}]^+$ and one each of a non-coordinating perchlorate anion and benzene molecule. Additional disordered methanol and water solvents occupied coordination sites and free space on the faces of the cobalt complex proximal and distal to the perchlorate anion. On the side of the complex proximal to the perchlorate, a hydrogen-bonded chain of three methanol molecules terminates in a hydrogen bond to a perchlorate oxygen atom. The cobalt-bound methanol shows

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positional disorder of the methyl groups. The distal side of the molecule was modeled as a three part disorder, using the SUMP command to ensure chemically reasonable disorder models and hydrogen bonding networks. The cobalt has either a water molecule or one of two positionally disordered methanol molecules bound. These are hydrogen bonded to a methanol on either side, as appropriate based on the O⁻H position. One of the hydrogen bonded methanols is also positionally disordered.

All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model, unless otherwise noted. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the Ueq value of the atoms they are linked to (1.5 times for methyl groups). The distance of all oxygen-bound methanol and water hydrogen atoms was fixed to 0.84 Å using distance restraints, and similarity restraints were placed on the carbon-hydrogen and cobalt-hydrogen distances for methanol, and the hydrogen-hydrogen distance for water was restrained to 1.33 Å. Carbon-cobalt 1,3 distances were also restrained with similarity restraints for the proximal Co-bound methanols. Finally, similar ADP restraints were employed for the distal side solvent molecules, as well as isotropic approximation restraints for the cobalt-bound distal methanols. The two proximal methanol carbons, c1b and c1c, required the ADPs to be constrained as equal.

Table 1 shows crystal data and structure refinement for SL001. Table 2 shows atomic coordinates and equivalent isotropic displacement parameters for SL001.

Table 1. Crystal data and structure refinement for SL001.

Identification code	SL001	
Empirical formula	C ₅₅ H ₃₅ Cl Co F ₂₀ N ₄ O _{9.49}	
Formula weight	1378.21	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 14.5161(16) Å	α = 60.248(2) °.
	b = 15.2922(19) Å	β = 74.322(3) °.
	c = 15.3546(19) Å	γ = 71.146(2) °.
Volume	2775.2(6) Å ³	
Z	2	

	Density (calculated)	1.649 Mg/m ³
	Absorption coefficient	0.487 mm ⁻¹
	F(000)	1386
	Crystal size	0.30 x 0.25 x 0.15 mm ³
5	Theta range for data collection	1.50 to 31.56°.
	Index ranges	-21<=h<=21, -22<=k<=22, -21<=l<=22
	Reflections collected	201135
	Independent reflections	18373 [R(int) = 0.0282]
	Completeness to theta = 31.56°	98.9 %
10	Absorption correction	Semi-empirical from equivalents
	Max. and min. transmission	0.9305 and 0.8676
	Refinement method	Full-matrix least-squares on F ²
	Data / restraints / parameters	18373 / 182 / 899
	Goodness-of-fit on F ²	1.029
15	Final R indices [I>2sigma(I)]	R1 = 0.0329, wR2 = 0.0855
	R indices (all data)	R1 = 0.0367, wR2 = 0.0881
	Largest diff. peak and hole	0.769 and -0.474 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for SL001. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

		x	y	z	U(eq)
5					
	Co(1)	2594(1)	8240(1)	9030(1)	10(1)
	N(1)	2649(1)	9479(1)	7733(1)	12(1)
	N(2)	2537(1)	9031(1)	9737(1)	12(1)
	N(3)	2537(1)	7003(1)	10326(1)	13(1)
10	N(4)	2634(1)	7450(1)	8331(1)	12(1)
	C(1)	3032(1)	8706(1)	6572(1)	13(1)
	C(2)	2893(1)	9530(1)	6780(1)	13(1)
	C(3)	2864(1)	10584(1)	6018(1)	18(1)
	C(4)	2560(1)	11174(1)	6517(1)	18(1)
15	C(5)	2447(1)	10479(1)	7584(1)	14(1)
	C(6)	2237(1)	10783(1)	8346(1)	13(1)
	C(7)	2321(1)	10088(1)	9356(1)	13(1)
	C(8)	2300(1)	10368(1)	10132(1)	15(1)
	C(9)	2559(1)	9473(1)	10968(1)	15(1)
20	C(10)	2689(1)	8643(1)	10723(1)	13(1)
	C(11)	2854(1)	7602(1)	11410(1)	14(1)
	C(12)	2722(1)	6848(1)	11230(1)	15(1)
	C(13)	2645(1)	5823(1)	12006(1)	20(1)
	C(14)	2382(1)	5369(1)	11570(1)	19(1)
25	C(15)	2343(1)	6097(1)	10518(1)	14(1)
	C(16)	2217(1)	5875(1)	9788(1)	13(1)
	C(17)	2392(1)	6509(1)	8753(1)	13(1)
	C(18)	2440(1)	6224(1)	7974(1)	17(1)
	C(19)	2753(1)	6976(1)	7085(1)	16(1)
30	C(20)	2848(1)	7751(1)	7307(1)	13(1)
	C(21)	3275(1)	8872(1)	5499(1)	13(1)
	C(22)	2545(1)	9176(1)	4912(1)	16(1)
	C(23)	2763(1)	9248(1)	3948(1)	16(1)
	C(24)	3727(1)	9027(1)	3542(1)	16(1)
35	C(25)	4473(1)	8737(1)	4096(1)	20(1)
	C(26)	4237(1)	8669(1)	5064(1)	18(1)

	C(27)	1973(1)	11913(1)	8054(1)	14(1)
	C(28)	1049(1)	12506(1)	7787(1)	17(1)
	C(29)	765(1)	13549(1)	7544(1)	20(1)
	C(30)	1421(1)	14024(1)	7558(1)	20(1)
5	C(31)	2351(1)	13462(1)	7806(1)	18(1)
	C(32)	2620(1)	12421(1)	8044(1)	15(1)
	C(33)	2436(1)	7291(1)	13233(1)	18(1)
	C(34)	2704(1)	6967(1)	14167(1)	21(1)
	C(35)	3681(1)	6612(1)	14296(1)	21(1)
10	C(36)	4391(1)	6576(1)	13500(1)	23(1)
	C(37)	4108(1)	6909(1)	12570(1)	20(1)
	C(38)	3128(1)	7274(1)	12415(1)	14(1)
	C(39)	1015(1)	4737(1)	10636(1)	15(1)
	C(40)	711(1)	3852(1)	10914(1)	17(1)
15	C(41)	1353(1)	3079(1)	10683(1)	18(1)
	C(42)	2291(1)	3185(1)	10206(1)	16(1)
	C(43)	2581(1)	4073(1)	9946(1)	15(1)
	C(44)	1944(1)	4885(1)	10130(1)	14(1)
	F(1)	1602(1)	9393(1)	5284(1)	30(1)
20	F(2)	2044(1)	9522(1)	3407(1)	27(1)
	F(3)	3939(1)	9082(1)	2615(1)	24(1)
	F(4)	5403(1)	8511(1)	3702(1)	41(1)
	F(5)	4971(1)	8376(1)	5589(1)	34(1)
	F(6)	398(1)	12067(1)	7761(1)	23(1)
25	F(7)	-125(1)	14097(1)	7285(1)	31(1)
	F(8)	1172(1)	15034(1)	7302(1)	30(1)
	F(9)	2984(1)	13935(1)	7803(1)	25(1)
	F(10)	3528(1)	11903(1)	8268(1)	21(1)
	F(11)	1482(1)	7618(1)	13134(1)	31(1)
30	F(12)	2024(1)	6986(1)	14948(1)	35(1)
	F(13)	3946(1)	6290(1)	15197(1)	31(1)
	F(14)	5335(1)	6232(1)	13636(1)	43(1)
	F(15)	4807(1)	6870(1)	11812(1)	36(1)
	F(16)	362(1)	5490(1)	10838(1)	20(1)
35	F(17)	-206(1)	3766(1)	11358(1)	24(1)
	F(18)	1063(1)	2238(1)	10905(1)	25(1)

	F(19)	2915(1)	2433(1)	9994(1)	22(1)
	F(20)	3503(1)	4136(1)	9505(1)	20(1)
	Cl(1)	-2992(1)	8176(1)	7157(1)	19(1)
	O(1A)	-3011(1)	8602(1)	7822(1)	26(1)
5	O(2A)	-2962(1)	7084(1)	7750(1)	35(1)
	O(3A)	-2148(1)	8352(1)	6399(1)	37(1)
	O(4A)	-3858(1)	8677(1)	6665(1)	33(1)
	C(1A)	8024(1)	6352(1)	5777(1)	27(1)
	C(2A)	8638(1)	5692(1)	5377(1)	31(1)
10	C(3A)	8248(1)	5301(1)	4944(1)	33(1)
	C(4A)	7248(1)	5579(1)	4901(1)	32(1)
	C(5A)	6634(1)	6231(1)	5311(1)	31(1)
	C(6A)	7023(1)	6618(1)	5751(1)	28(1)
	O(1B)	1192(1)	8648(1)	9099(1)	18(1)
15	C(1B)	516(1)	8381(2)	10001(1)	27(1)
	C(1C)	466(6)	8937(11)	9760(8)	27(1)
	O(2B)	485(1)	9122(1)	7550(1)	27(1)
	C(2B)	194(1)	10210(1)	6980(1)	35(1)
	O(3B)	-361(1)	8309(1)	6850(1)	33(1)
20	C(3B)	167(1)	7767(1)	6269(1)	35(1)
	O(4B)	3986(1)	7871(1)	8962(1)	19(1)
	C(4C)	4555(4)	8675(5)	8636(6)	35(2)
	C(4D)	4666(4)	6996(5)	8870(9)	63(3)
	O(5B)	4917(1)	9244(1)	8515(1)	36(1)
25	C(5B)	4999(1)	9359(2)	9359(2)	32(1)
	O(6B)	5050(7)	6648(6)	8153(6)	38(1)
	C(6B)	5075(3)	5599(3)	8957(6)	57(2)
	O(6C)	5181(8)	6480(9)	8462(9)	49(2)
30	C(6C)	5030(4)	5856(5)	8104(6)	47(2)

Device Characterization

Devices were fabricated by drop-casting a suspension of SWCNTs and the desired porphyrin complex between gold electrodes (1 mm gap) in a 14-channel array with a shared counter-electrode, a design for simultaneous measurement with different composites. See, for example, J. M. Schnorr, et al., *Adv. Funct. Mater.* **2013**, 23, 5285–5291, which is incorporated by

reference in its entirety. The responses to various concentrations of NH_3 can be calibrated. Low concentrations of NH_3 diluted in N_2 were delivered to the device while a potentiostat applied 0.100 V across the electrodes and recorded current. Negative change in current resulting from exposure to NH_3 was divided by initial current to give change in conductance ($-\Delta G/G_0$), which was taken as the response.

FIG. 2A shows the average responses for two devices of each of the materials to three 30 s exposures to NH_3 . The responses are approximately linear below 10 ppm, at which they appear to saturate. The responses change from irreversible to semi-reversible around this concentration as seen in FIG. 2B, which shows the baseline-corrected conductance traces of a [Co(tpfpp)] ClO_4 -based device responding to NH_3 . The device can detect less than 0.5 ppm NH_3 . Their sensitivity toward NH_3 is more than an order of magnitude greater than that of pristine SWCNTs.

Sensitivity to amines can improve with increased electron deficiency at the Co center. Using the first reduction potential of the complexes as a proxy for electron deficiency, the correlation between sensitivity to NH_3 and electron deficiency at the Co center can be investigated. FIG. 3 shows the response of the Co composites to 20 ppm NH_3 against the first reduction potential of the Co complex. These results suggest that efficacy for NH_3 detection in this system improves with increasing electron deficiency at the metal center.

For monitoring meat spoilage, the detection of BAs such as putrescine and cadaverine is pertinent. FIGS. 4 shows the responses of [Co(tpfpp)] ClO_4 -SWCNT chemiresistors to exposures of both putrescine (FIG. 4A) and cadaverine (FIG. 4B). The strong responses are dosimetric and can find utility in single-use wireless tags. See, for example, J. M. Azzarelli, et al., Proc. Natl. Acad. Sci. USA 2014, 111, 18162–18166, which is incorporated by reference in its entirety.

Detection of BAs in meat samples requires a strategy for distinguishing them from the complex matrix. To assess their selectivity toward amines, responses of [Co(tpp)] ClO_4 -SWCNT devices to volatile compounds representing a wide range of functional groups can be measured (FIG. 5). The devices exhibit high selectivity for NH_3 among the analytes tested. Species capable of simply coordinating to the Co^{3+} center (e.g., H_2O , EtOH, THF, CO) do not elicit a strong response, suggesting that charge transfer is a large component of signal transduction for amines in this system. While the devices alone cannot distinguish amines from each other, their response will reflect the TVBN level with minor contribution from interferents.

The detector can be used to compare TVBN emission from day to day for 1.0 g aliquots of various types of raw meat: pork, chicken, salmon, and cod. A sample was placed in a gas flow chamber. See, for example, B. Esser, et al., *Angew. Chem.* 2012, 124, 5851-5855; B. Esser, et al., *Angew. Chem. Int. Ed.* 2012, 51, 5752-5756, each of which is incorporated by reference in its entirety. N₂ (0.25 L/min) was passed alternately over the detector or first through the chamber holding the meat sample at 25 °C before passing over the detector. The initial peak response at the end of a 30 s exposure was not as reproducible as the ΔG values taken 60 s after the end of the exposure (FIG. 6A). This effect may be the result of unknown interfering analytes that give a reversible sensor response. As shown in FIG. 4, target BAs are likely to give irreversible responses over time periods reflected in this scheme. Hence, the delay gives a more faithful measurement of these key BAs.

The results of the meat monitoring measurements made with the same [Co(tpp)]ClO₄-based device across 4 days are shown in FIG. 6B. Two samples for each meat were monitored, one stored at room temperature (22 °C) and one at 4 °C. For samples stored at 4 °C, the detector showed no increase in response over 4 days. The absence of observable spoilage for meat samples stored for 4 days at 4 °C is consistent with the literature. For samples stored at 22 °C, an increase in response was observed after day 1, and even greater responses were recorded by day 4; this increase in TVBN content between days 1 and 2 and further increase after day 2 is consistent with literature reports for BA levels in meat determined using other techniques (electrochemistry, chromatography, and spectrometry). See, for example, G. C. Chemnitius, et al., *Sens. Actuators, B* 1996, 32, 107-113, which is incorporated by reference in its entirety.

Chemiresistive detectors for amines can be created from single-walled carbon nanotubes by non-covalent modification with cobalt meso-arylporphyrins. With changes in oxidation state, electron-withdrawing character of the porphyrin ligand, and counteranion, the response to ammonia can be improved. The devices can have sub-ppm sensitivity and high selectivity toward amines. The detectors can be used in monitoring meat spoilage.

Gas Detection Measurements

Gas detection measurements were acquired by using a test clip fitted with a PTFE spacer to connect the gold electrodes of the device to a PalmSens EmStat potentiostat with a MUX16 multiplexer. For ammonia detection measurements, the chemiresistive device was enclosed in a

PTFE chamber, and a gas mixer system was used to deliver to the chamber low concentrations of ammonia gas diluted by nitrogen. The gas mixer was comprised of two digital mass flow controllers purchased from Sierra Instruments. A MicroTrak Mass Flow Controller is used to deliver up to 4 mL/min of a mixture of 1% ammonia in nitrogen that was further diluted in the gas mixer by nitrogen delivered by the other MFC at 2.00 L/min. The potentiostat was used to apply a constant potential of 0.100 V across the electrodes, and the current was recorded using PSTrace software (v. 3.0) as the device was exposed to varying concentrations of ammonia for 30 s at a time with at least 70 s between successive measurements. Carbon monoxide measurements were made in a similar manner, using CO in the place of the 1% NH₃ in nitrogen.

For measuring device response to volatile liquid organic compounds and to water, a KIN-TEK gas generator system was used after calibration for each compound. Data for amine detection measurements were corrected to a linear fit of the baseline current that was measured prior to gas exposures; for other analytes, the data were corrected to a linear fit of the baseline across the entire data acquisition time.

As their parent Co complexes are air-stable, the devices fabricated from them can be stable to oxidation by molecular oxygen in ambient conditions. Using representative [Co(tp⁺)][ClO₄]⁻ based devices, to assess their stability toward oxygen, NH₃ detection measurements using air as the carrier gas were performed and compared to measurements made with the same devices using nitrogen as the carrier gas. As shown in FIG. 16A, the responses to NH₃ are negligibly affected by performing the measurements in the presence of oxygen. Likewise, as the Co porphyrin complexes are synthesized and used as their aquo adducts, device performance can be unaffected by exposure to water. Devices fabricated from [Co(tp⁺)][ClO₄]⁻ were placed in water-saturated air at 30 °C (4 kPa H₂O) for 10 and 40 min and then tested for their response to NH₃. FIG. 16B shows that this exposure to moisture did not negatively affect the device performance. FIG. 16C shows that storage under ambient conditions for two weeks also does not negatively affect device performance. FIG. 18 shows that halving the mass of the meat will also halve the detector's response, demonstrating that this experimental setup is dependent on the mass of the meat sample and not at saturation.

Other embodiments are within the scope of the following claims.

WHAT IS CLAIMED IS:

1. A sensor comprising:

5 a conductive region in electrical communication with at least two electrodes, the conductive region including a complex, wherein the complex includes a carbon nanotube that is functionalized by a porphyrin.

2. The sensor of claim 1, wherein the porphyrin includes a cobalt porphyrin.

10 3. The sensor of claim 2, wherein the cobalt porphyrin includes a Co^{3+} .

4. The sensor of claim 2, wherein the cobalt porphyrin includes a Co^{2+} .

15 5. The sensor of claim 1, wherein the carbon nanotube is non-covalently functionalized by the porphyrin.

6. The sensor of claim 1, wherein the carbon nanotube is covalently functionalized.

20 7. The sensor of claim 1, wherein the complex includes a cobalt *meso*-arylporphyrin complex.

8. The sensor of claim 1, wherein the complex includes a *meso*-tetrakis(pentafluorophenyl)porphyrinato.

25 9. The sensor of claim 1, wherein the complex includes a *meso*-tetraphenylporphyrinato.

10. The sensor of claim 1, wherein the complex includes a *meso*-arylporphyrin.

11. The sensor of claim 1, wherein the porphyrin includes a ClO_4^- .

30 12. The sensor of claim 1, wherein the porphyrin includes a BF_4^- .

13. The sensor of claim 1, wherein the porphyrin includes a Cl⁻.

14. The sensor of claim 1, wherein the carbon nanotube is a single-walled carbon nanotube.

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15. A method of sensing an analyte comprising:

exposing a sensor to a sample, the sensor including:

a conductive region in electrical communication with at least two electrodes, the

conductive region including a complex, wherein the complex includes a carbon

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nanotube that is functionalized by a porphyrin; and

measuring an electrical property at the electrodes.

16. The method of claim 15, further comprising detecting an amine.

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17. The method of claim 15, further comprising detecting a putrescine.

18. The method of claim 15, further comprising detecting a cadaverine.

19. The method of claim 15, wherein the detection is semi-reversible.

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20. The method of claim 15, further comprising detecting the analyte below 0.5 ppm.

21. The method of claim 15, further comprising detecting the analyte below 1 ppm.

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22. The method of claim 15, further comprising detecting the analyte wirelessly.

23. The method of claim 15, further comprising detecting the analyte through a wireless radio frequency communication.

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24. The method of claim 15, further comprising detecting an output from a radio frequency identification tag including the sensor.

25. The method of claim 15, further comprising detecting nitrogen content.

26. The method of claim 15, further comprising non-covalently functionalizing the carbon
5 nanotube.

27. The method of claim 15, further comprising covalently functionalizing the carbon
nanotube.

10 28. The method of claim 15, further comprising providing an irreversible response to one or
more nitrogen bases.

29. A method of preparing a sensor comprising:

15 forming a complex including a conductive region in electrical communication with
at least two electrodes, the conductive region including a complex, wherein the complex
includes a carbon nanotube that is functionalized by a porphyrin; and
placing the conductive material in electrical communication with at least two
electrodes.

20 30. A food packaging comprising a sensor, wherein the sensor includes a conductive region in
electrical communication with at least two electrodes, the conductive region including a
complex, wherein the complex includes a carbon nanotube that is functionalized by a
porphyrin.

25

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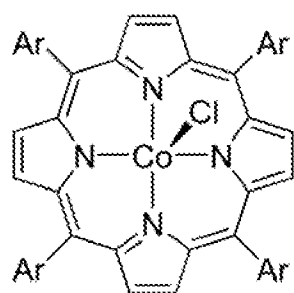
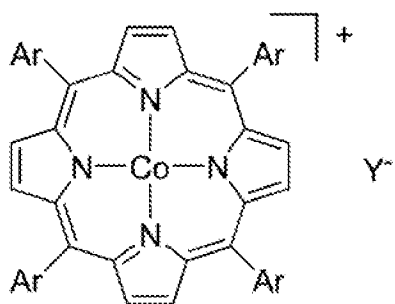
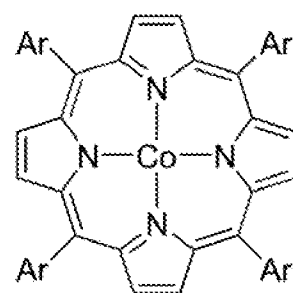
Ar = C₆H₅, [Co(tp_p)Cl]Ar = C₆F₅, [Co(tpf_{pp})Cl]Ar = C₆H₅, Y⁻ = ClO₄⁻, [Co(tp_p)]ClO₄Ar = C₆F₅, Y⁻ = ClO₄⁻, [Co(tpf_{pp})]ClO₄Ar = C₆H₅, Y⁻ = BF₄⁻, [Co(tp_p)]BF₄Ar = C₆H₅, [Co(tp_p)]Ar = C₆F₅, [Co(tpf_{pp})]

FIG. 1

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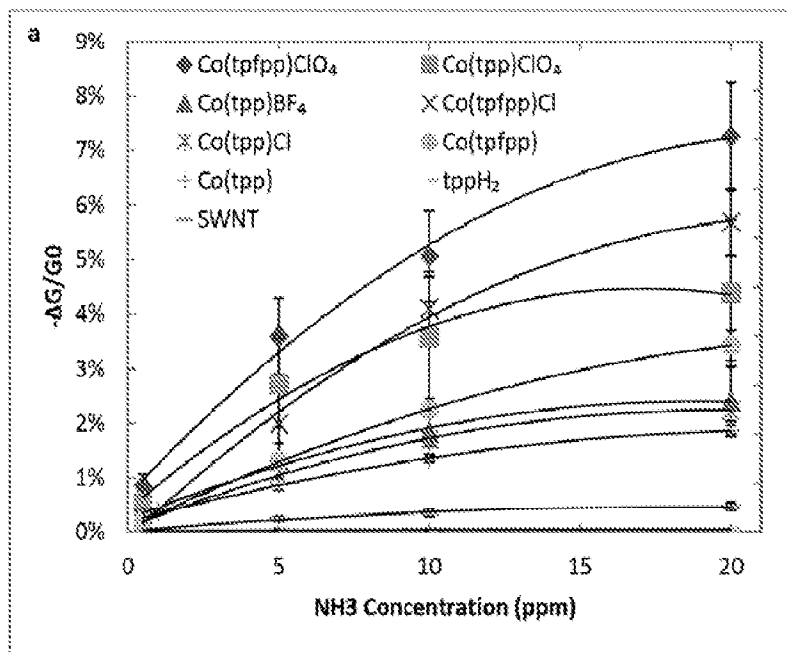


FIG. 2A

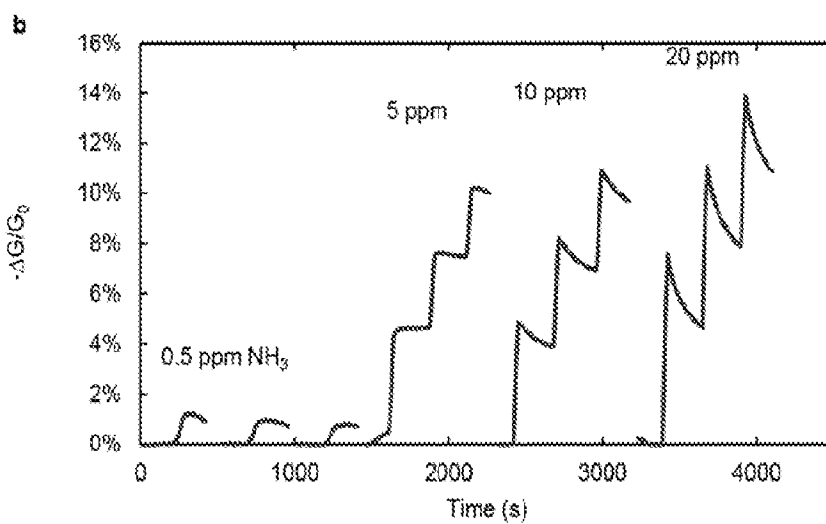


FIG. 2B

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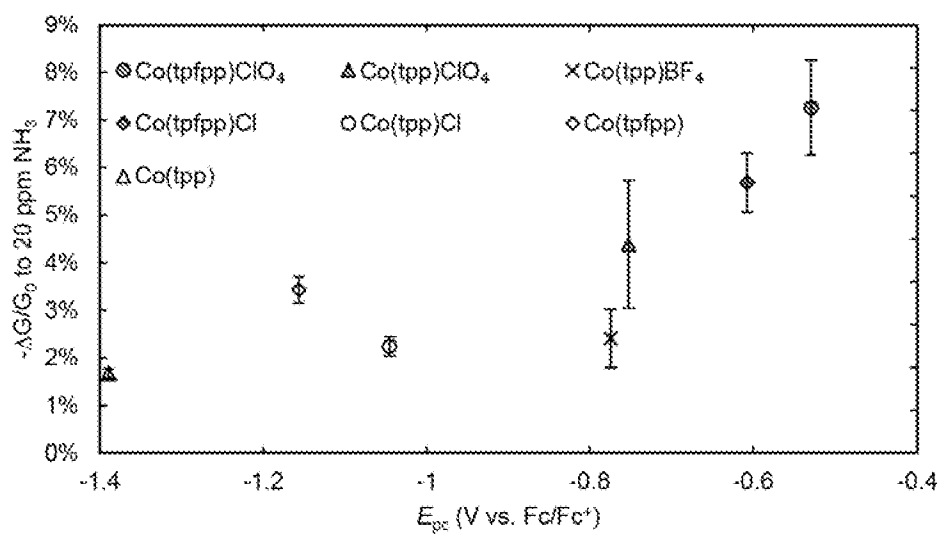


FIG. 3

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a

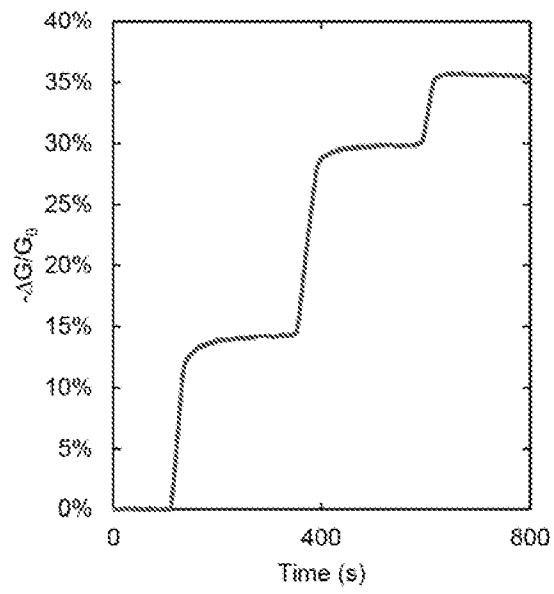


FIG. 4A

b

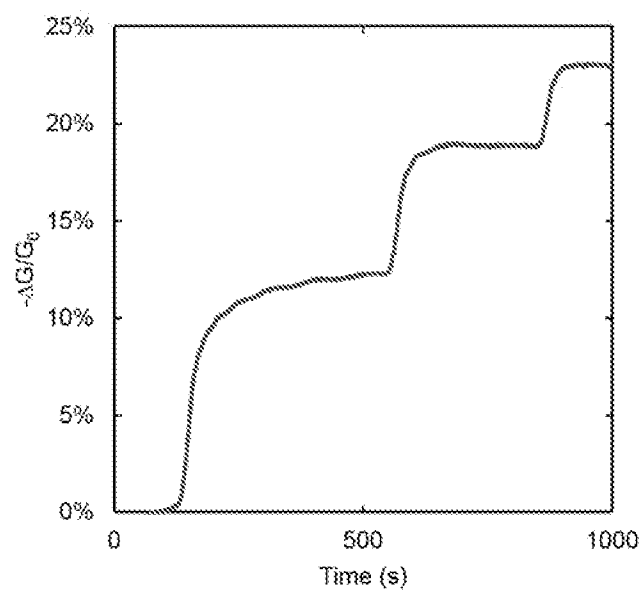


FIG. 4B

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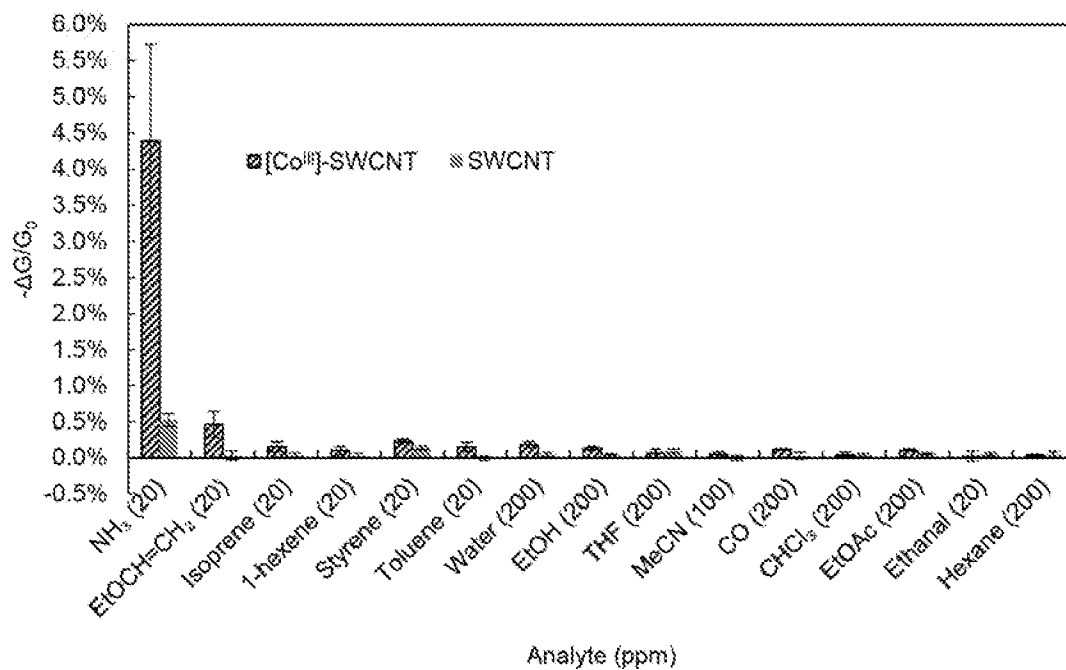


FIG. 5

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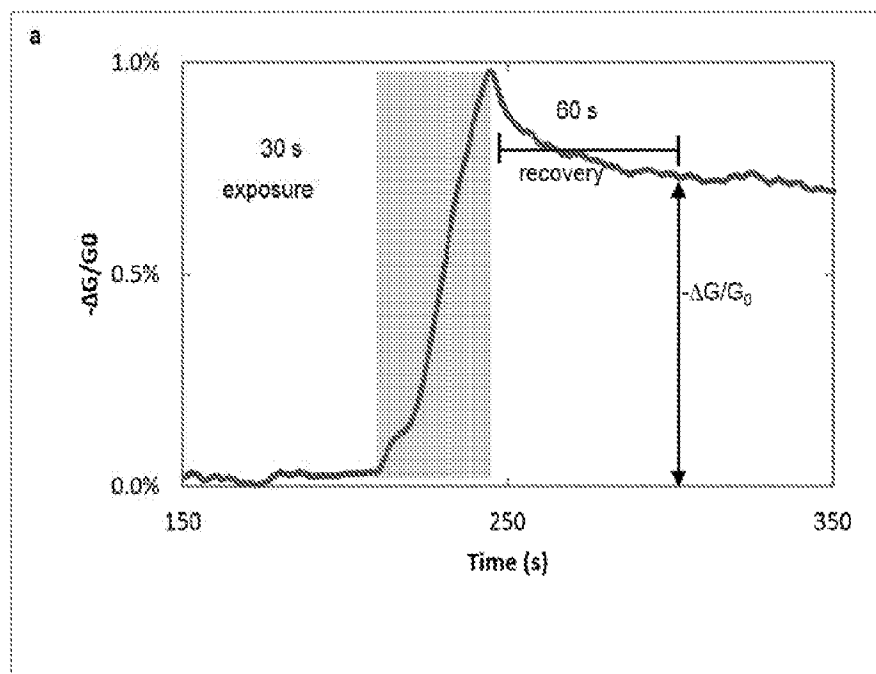


FIG. 6A

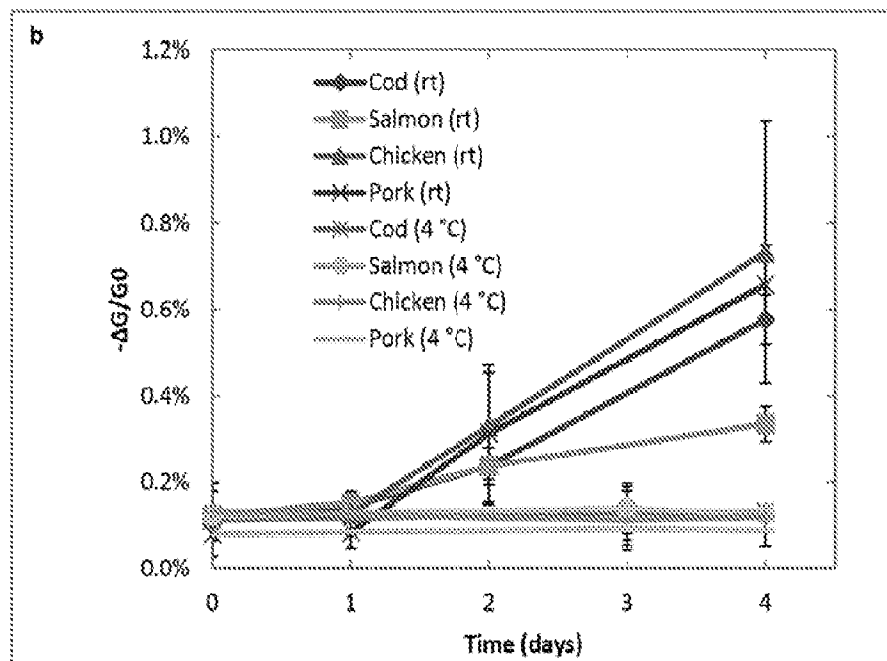


FIG. 6B

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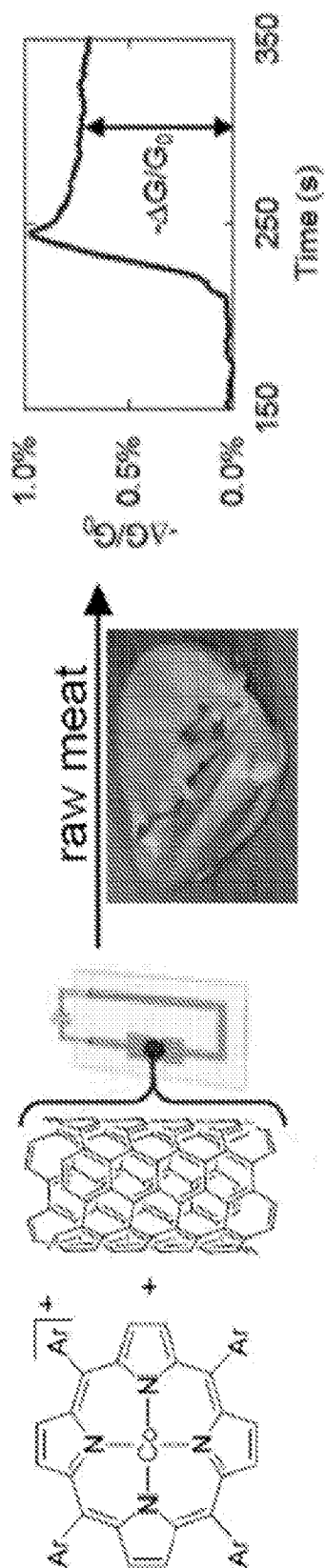


FIG. 7

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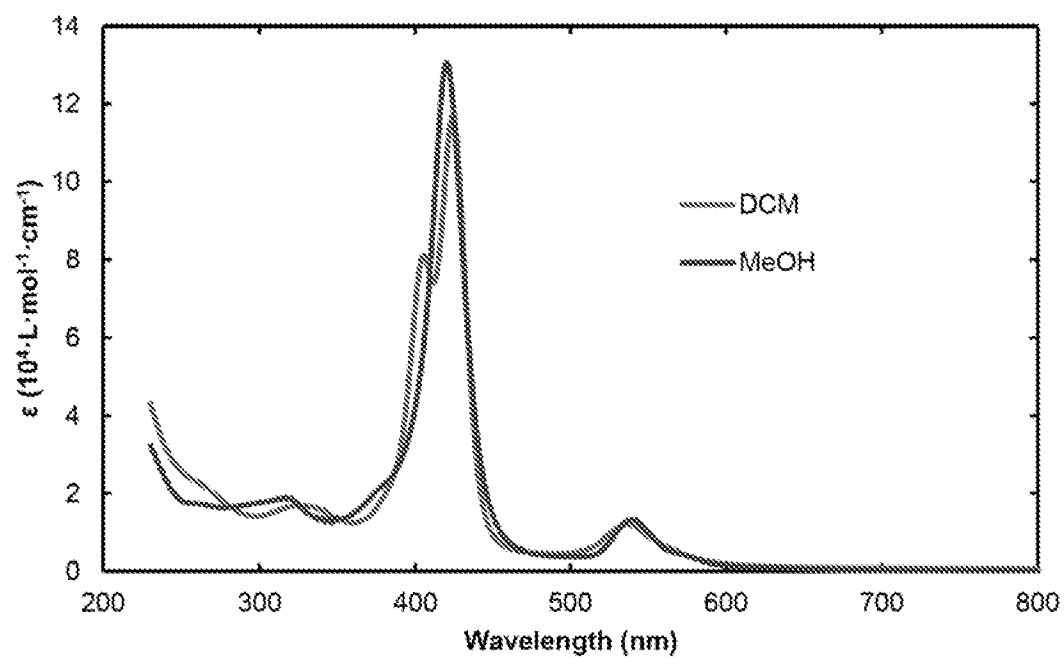


FIG. 8

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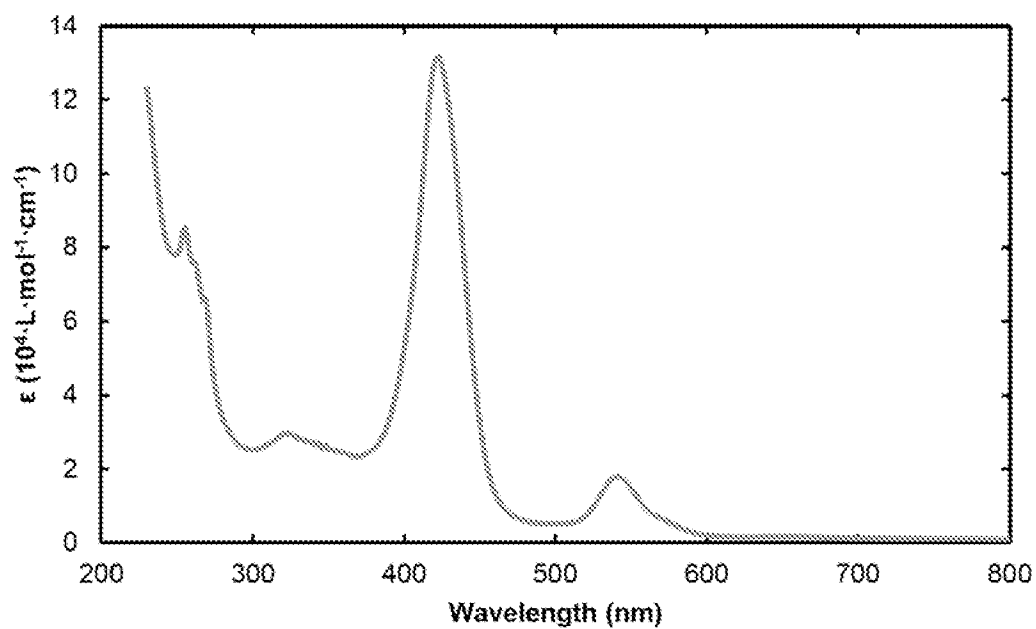


FIG. 9

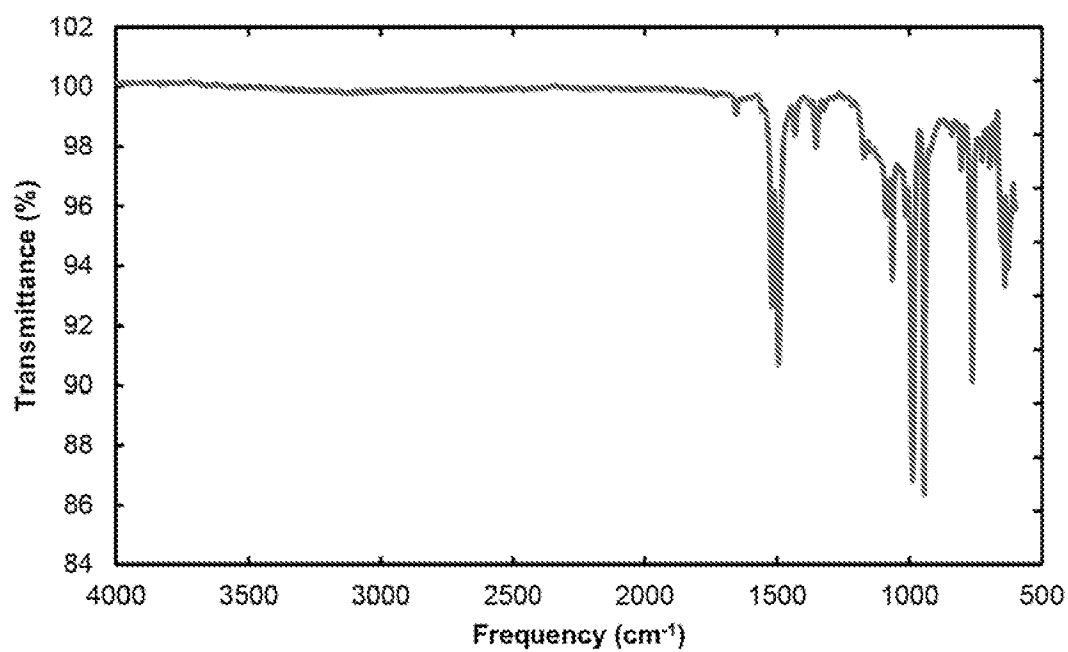


FIG. 10

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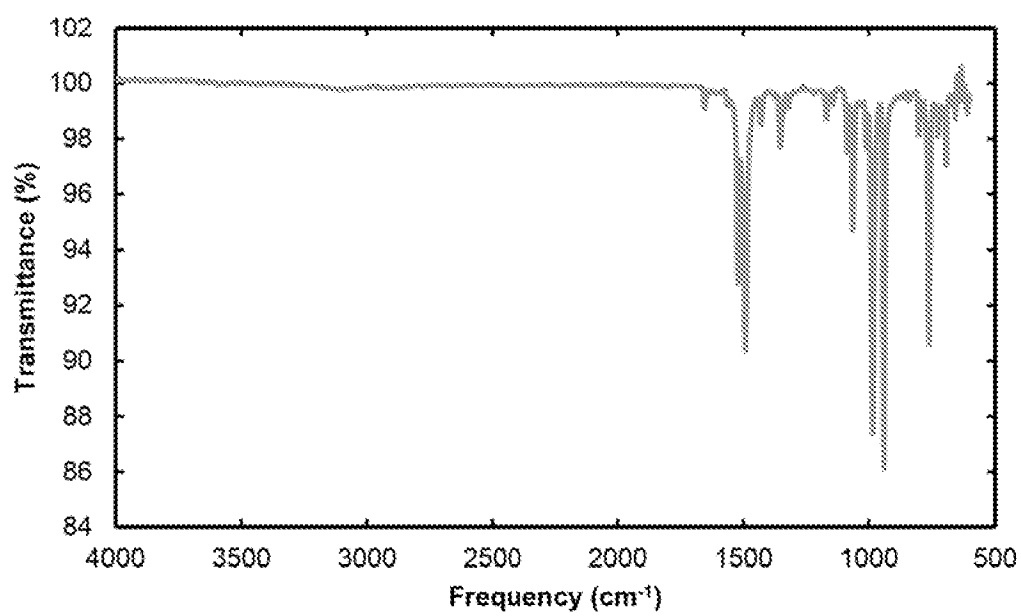


FIG. 11

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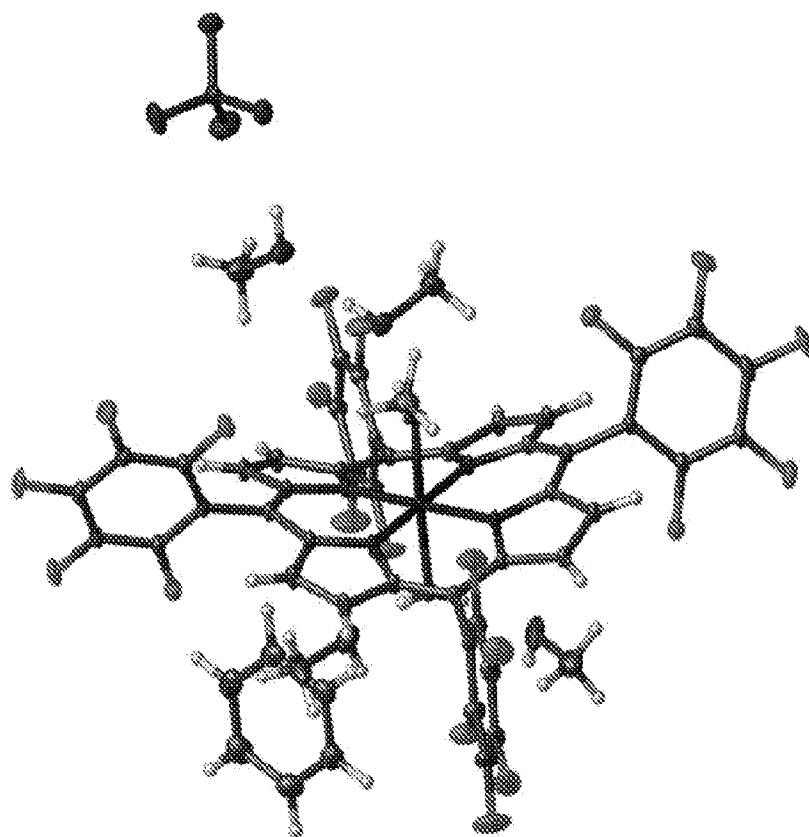


FIG. 12

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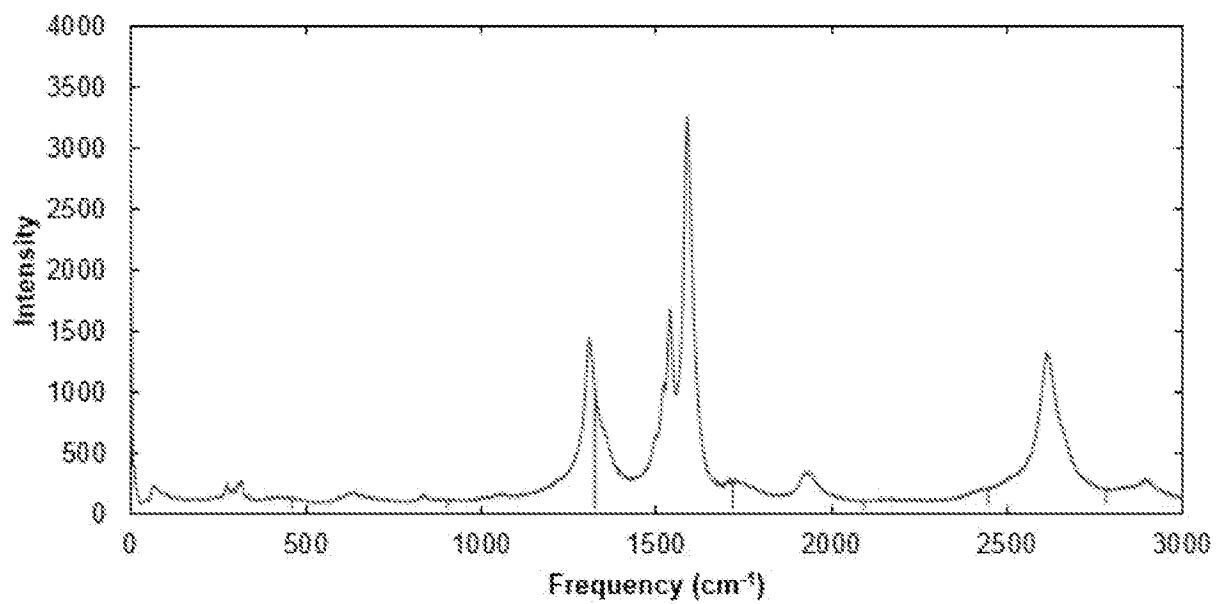


FIG. 13

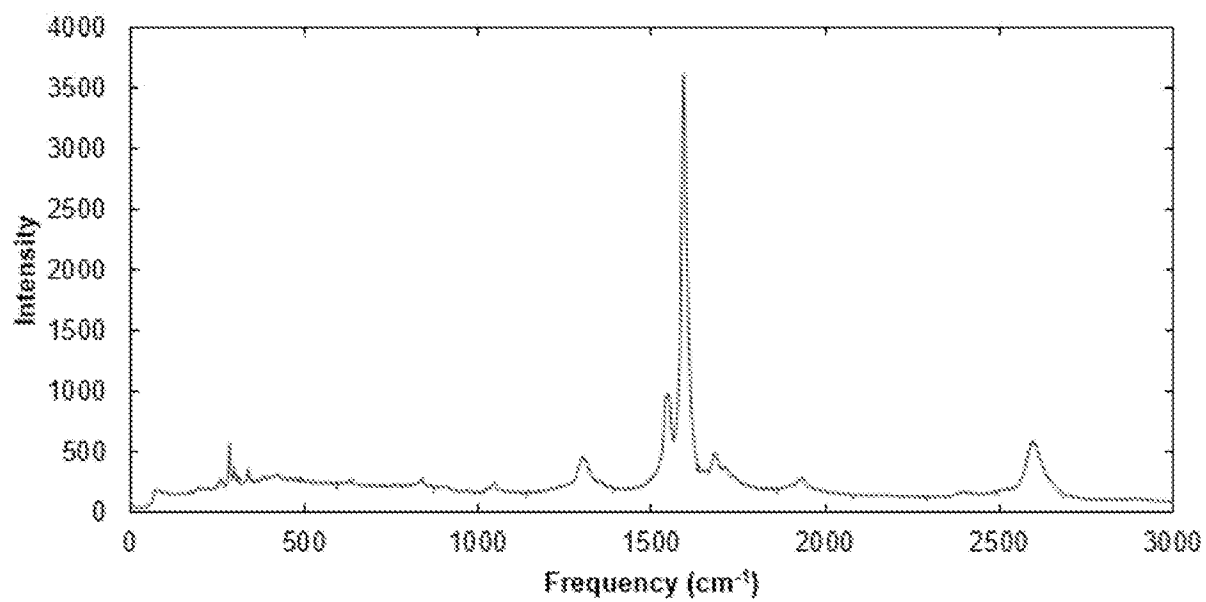


FIG. 14

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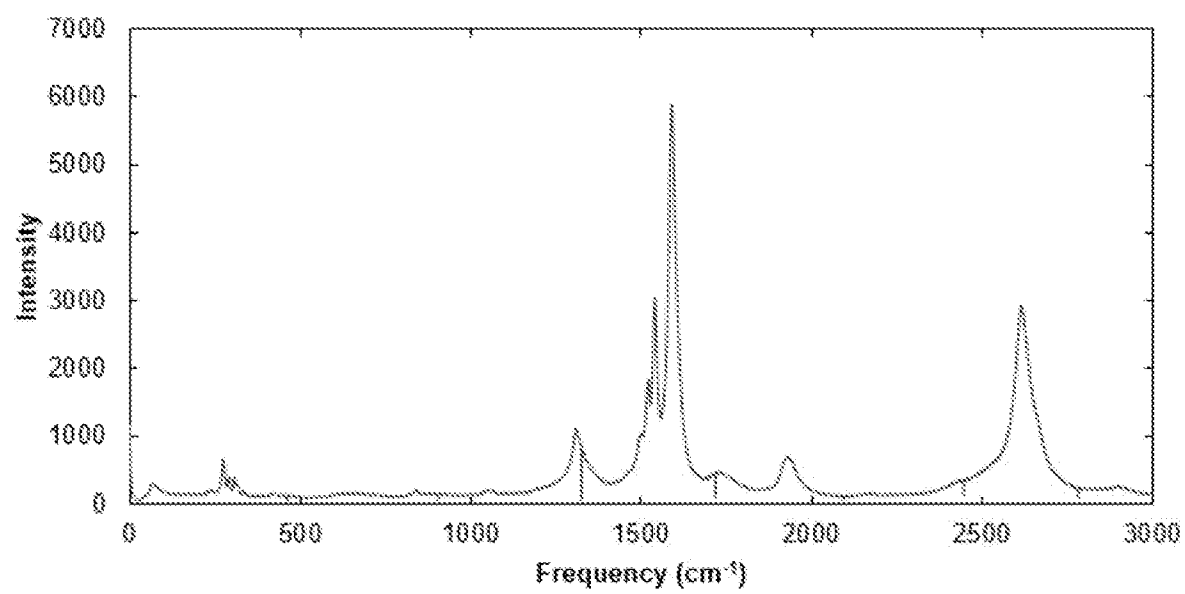


FIG. 15

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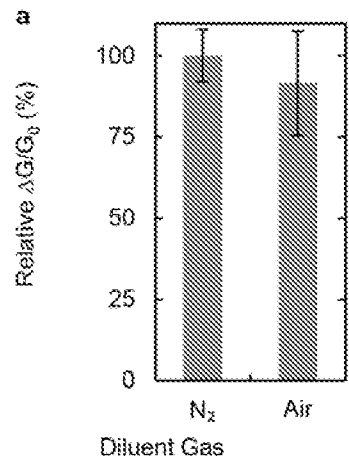


FIG. 16A

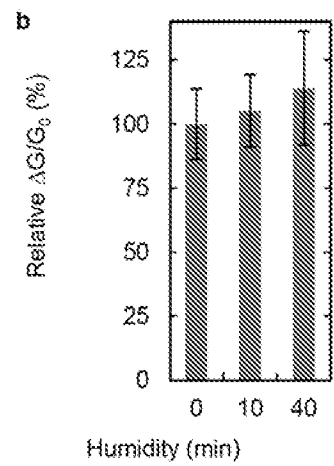


FIG. 16B

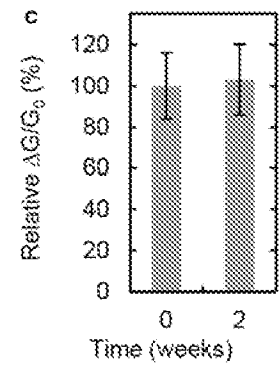


FIG. 16C

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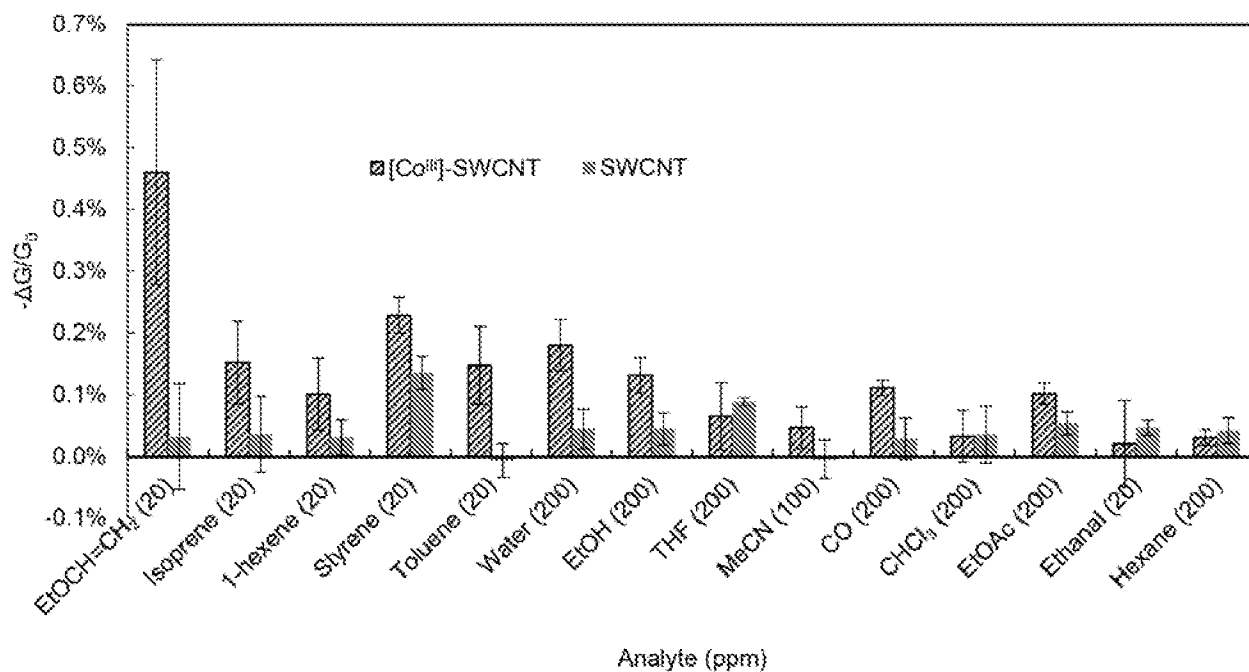


FIG. 17

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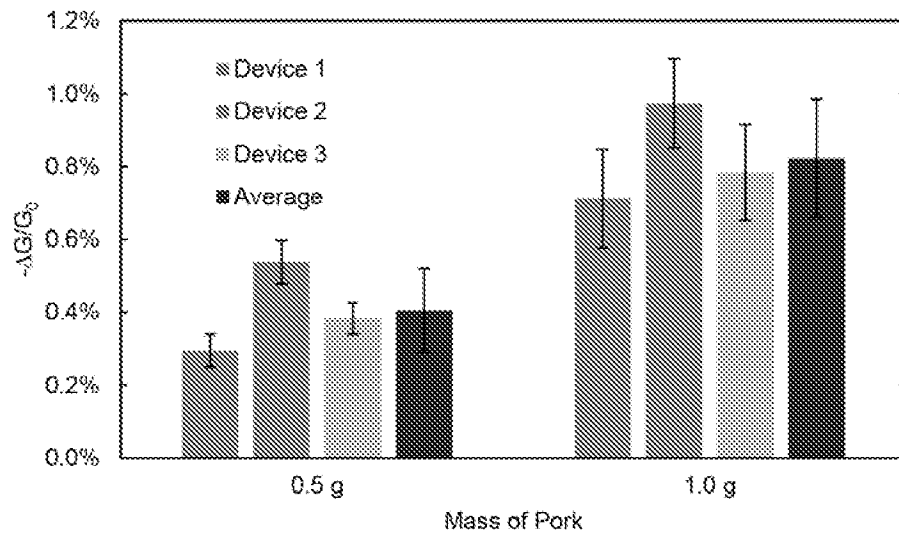


FIG. 18

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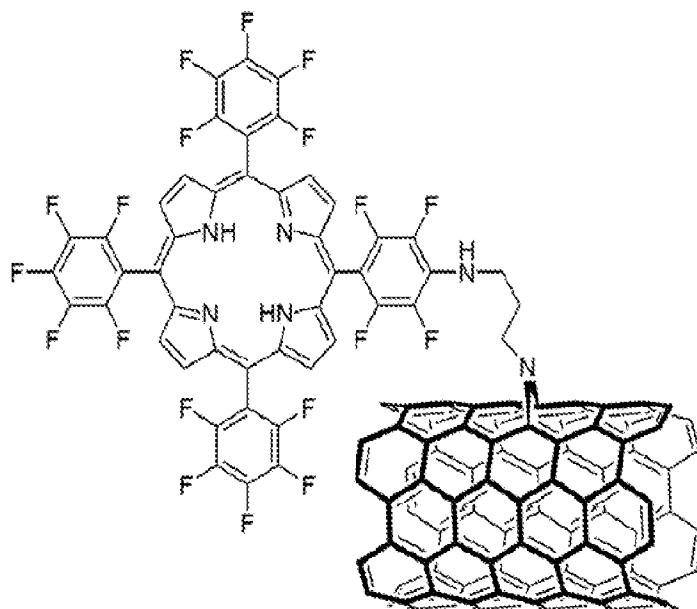


FIG. 19

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2016/025790

A. CLASSIFICATION OF SUBJECT MATTER

INV. G01N27/12 G01N33/12
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

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)

EPO-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	MAHENDRA D. SHIRSAT ET AL: "Porphyrin-Functionalized Single-Walled Carbon Nanotube Chemiresistive Sensor Arrays for VOCs", JOURNAL OF PHYSICAL CHEMISTRY C, vol. 116, no. 5, 9 February 2012 (2012-02-09), pages 3845-3850, XP055277297, US	1,5,6,9, 10,14, 15, 19-21, 26,27,29
Y	ISSN: 1932-7447, DOI: 10.1021/jp210582t abstract page 3846, column 1, paragraph 1 - page 3848, column 1, paragraph 1; figure 4 ----- -/--	2,4,7,8, 13, 16-18,25



Further documents are listed in the continuation of Box C.



See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search

6 June 2016

Date of mailing of the international search report

17/06/2016

Name and mailing address of the ISA/

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Lazar, Zala

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2016/025790

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	NEAL A. RAKOW ET AL: "Molecular Recognition and Discrimination of Amines with a Colorimetric Array", ANGEWANDTE CHEMIE INTERNATIONAL EDITION, vol. 44, no. 29, 18 July 2005 (2005-07-18), pages 4528-4532, XP055277408, DE ISSN: 1433-7851, DOI: 10.1002/anie.200500939 page 4529, column 1, paragraph 1 - page 4531, column 2, paragraph 3; figures 1,2,5 & Neal A. Rakow: "Supporting Information", 18 July 2005 (2005-07-18), XP055277407, Retrieved from the Internet: URL: http://www.readcube.com/articles/supplement?doi=10.1002~2Fanie.200500939&index=0&parent_url=1&preview=1 [retrieved on 2016-06-02] figure S1 -----	2,4,7, 13,16-18
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Y	US 2004/157281 A1 (HULKOWER KEREN I [US] ET AL) 12 August 2004 (2004-08-12) paragraphs [0041], [0053] - [0059]; figure 1 -----	16-18,25
Y	US 2005/153052 A1 (WILLIAMS JOHN R [US] ET AL) 14 July 2005 (2005-07-14) abstract sentences 1,24-28 -----	8
Y	US 2005/153052 A1 (WILLIAMS JOHN R [US] ET AL) 14 July 2005 (2005-07-14) abstract sentences 1,24-28 -----	30
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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2016/025790

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2005/248455 A1 (POPE GARY W [US] ET AL) 10 November 2005 (2005-11-10) abstract paragraphs [0003], [0010] -----	22-24
Y	HIROSHI SUGIMOTO ET AL: "Preparation and physicochemical properties of tervalent cobalt complexes of porphyrins.", BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, vol. 54, no. 11, 1 January 1981 (1981-01-01), pages 3425-3432, XP055277397, JP ISSN: 0009-2673, DOI: 10.1246/bcsj.54.3425 abstract page 3425, column 2, paragraph 1 -----	3,11-13
X	PENZA M ET AL: "Metalloporphyrins-modified carbon nanotubes networked films-based chemical sensors for enhanced gas sensitivity", SENSORS AND ACTUATORS B, vol. 144, no. 2, 17 February 2010 (2010-02-17), pages 387-394, XP026888317, ISSN: 0925-4005, DOI: 10.1016/J.SNB.2008.12.060 [retrieved on 2009-01-06] abstract page 387, column 2, paragraph 4 - page 392, column 1, paragraph 1; figures 3,4,8,10,11 -----	1,5,9, 10,15, 16,25, 26,28,29
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/025790

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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