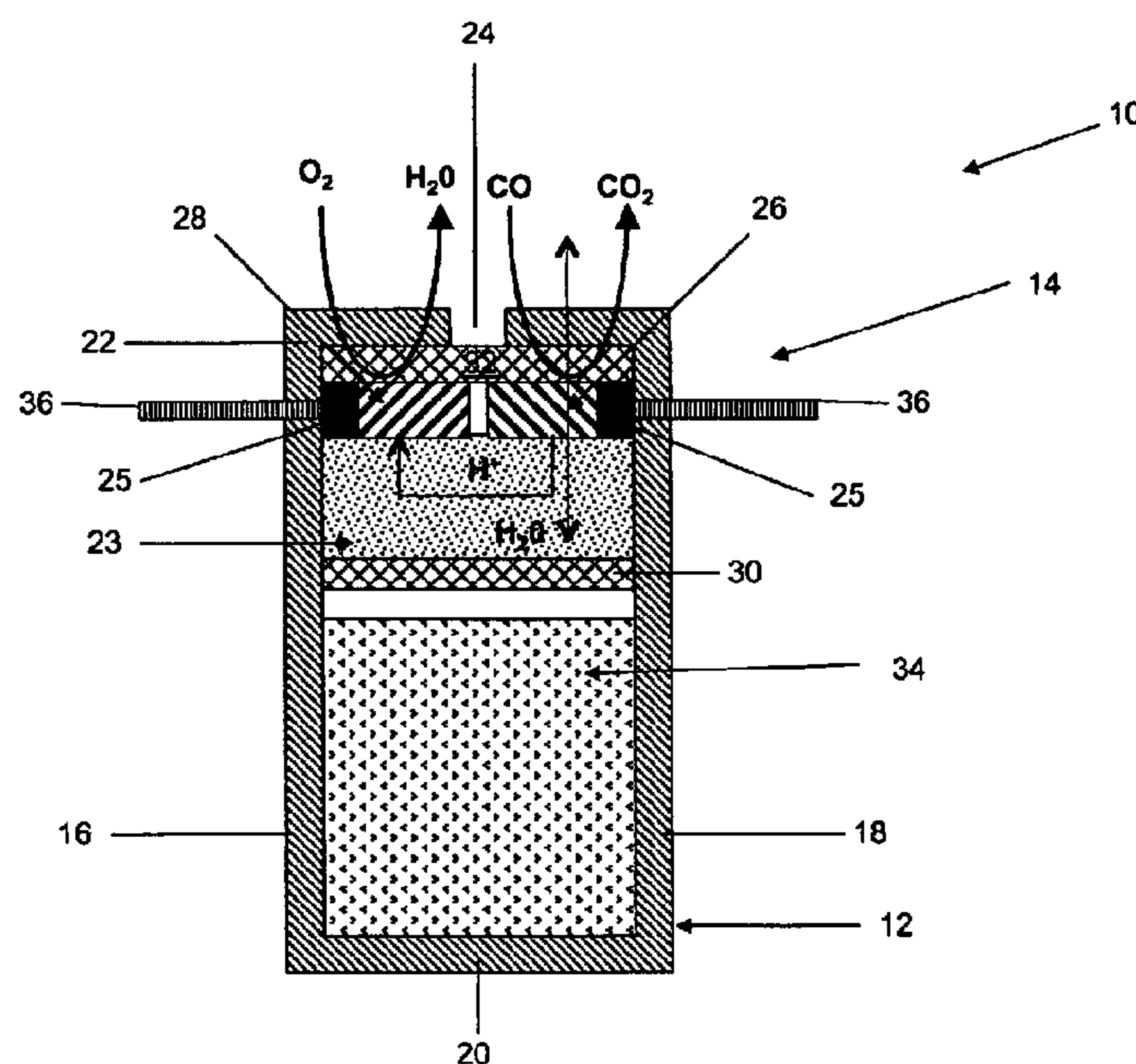




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(54) **Titre : MATERIAUX CATHODIQUES DESTINES A ETRE UTILISES DANS DES CAPTEURS ELECTROCHIMIQUES ET DISPOSITIFS ASSOCIES ET PROCEDES DE FABRICATION DE CES DERNIERS**
(54) **Title: CATHODIC MATERIALS FOR USE IN ELECTROCHEMICAL SENSORS AND ASSOCIATED DEVICES AND METHODS OF MANUFACTURING THE SAME**



(57) **Abbrégé/Abstract:**

A cathodic material for use in an electrochemical sensor comprising: a carbonaceous material and an oxygen reduction catalyst associated with the carbonaceous material; and wherein the cathodic material does not materially exhibit catalytic activity for the oxidation of carbon monoxide. Associated electrochemical sensors may include an anode and cathode that are disposed upon the same or opposite sides of an ion exchange membrane and/or exposed to the same or different gaseous environments.



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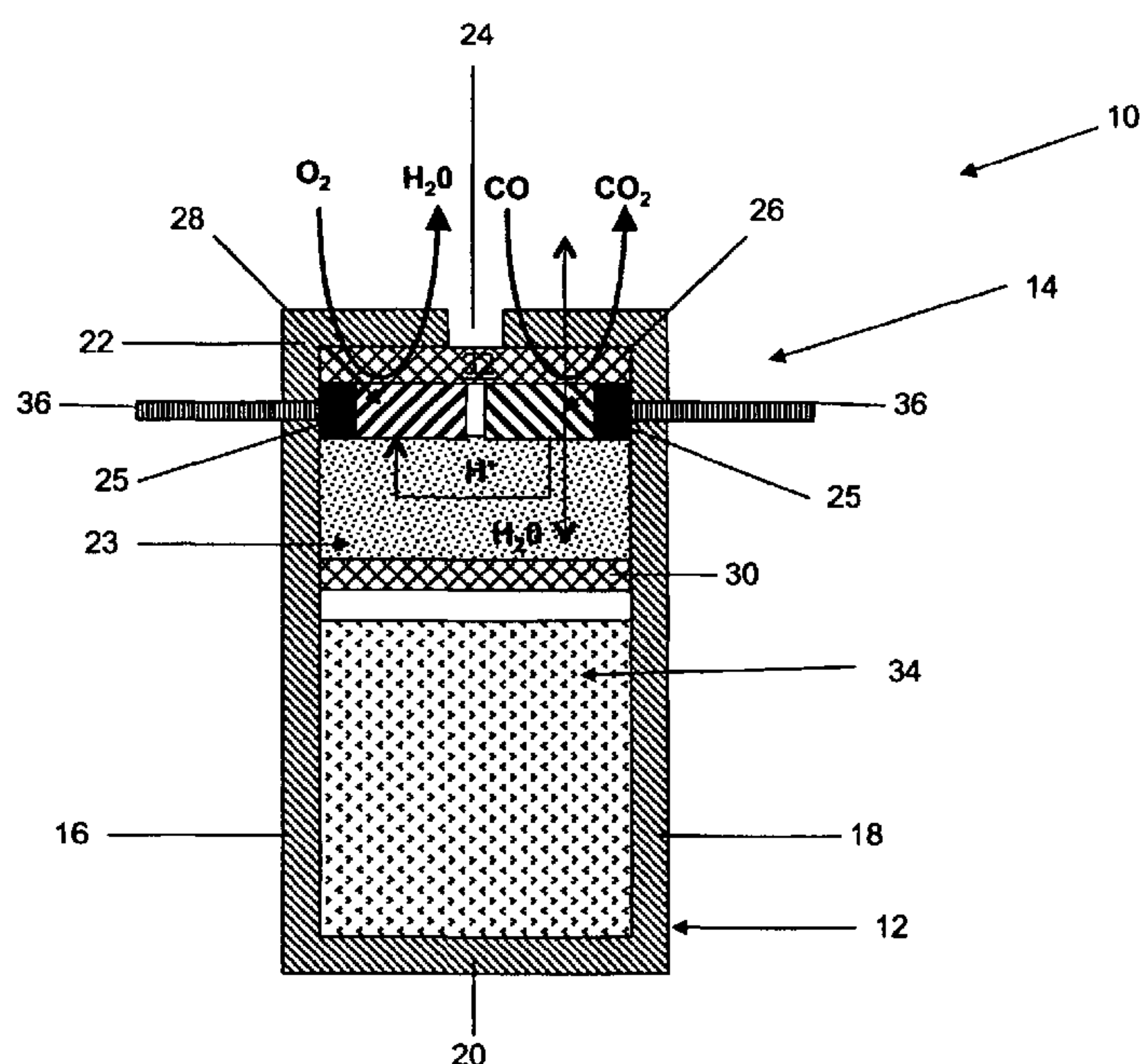
(54) Title: CATHODIC MATERIALS FOR USE IN ELECTROCHEMICAL SENSORS AND ASSOCIATED DEVICES AND
METHODS OF MANUFACTURING THE SAME

Figure 1A

(57) Abstract: A cathodic material for use in an
electrochemical sensor comprising: a carbonaceous
material and an oxygen reduction catalyst associated
with the carbonaceous material; and wherein the cathodic
material does not materially exhibit catalytic
activity for the oxidation of carbon monoxide. Associated
electrochemical sensors may include an anode and cathode
that are disposed upon the same or opposite sides of an ion
exchange membrane and/or exposed to the same or different
gaseous environments.

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TITLE OF THE INVENTION

CATHODIC MATERIALS FOR USE IN ELECTROCHEMICAL SENSORS AND
ASSOCIATED DEVICES AND METHODS OF MANUFACTURING THE SAME

5

10 **BACKGROUND OF THE INVENTION**

1. Field of the Invention

[0001] The present invention relates in general to cathodic materials for use in fuel cells and electrochemical sensors and, more particularly, to carbonaceous materials associated with oxygen reduction catalysts, for example, substituted and unsubstituted transition metal porphyrins, substituted and unsubstituted transition metal tetrabenzoporphyrins, substituted and unsubstituted transition metal tetraphenylporphyrins, substituted and unsubstituted transition metal tetraazaporphyrins, substituted and unsubstituted transition metal tetraazamacrocycles, substituted and unsubstituted transition metal phthalocyanines, substituted and unsubstituted transition metal naphthalocyanines, substituted and unsubstituted transition metal bis(phthalocyanines), substituted and unsubstituted transition metal bis(naphthalocyanines), and combinations thereof. The present invention further relates to fuel cells and electrochemical sensors having novel structural configurations, wherein the anode and the cathode of an associated micro electrode assembly (MEA) are disposed upon the same side or different sides of an ion exchange membrane, and/or exposed to the same gaseous environment or different gaseous environments – among

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other configurations. The present invention also relates to gas, smoke and/or fire detectors comprising novel electrochemical sensors, micro electrode assemblies, and/or sub-components for the same, as well as associated methods of manufacturing.

2. Background Art

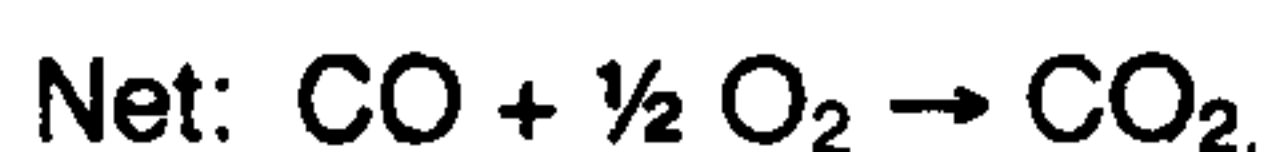
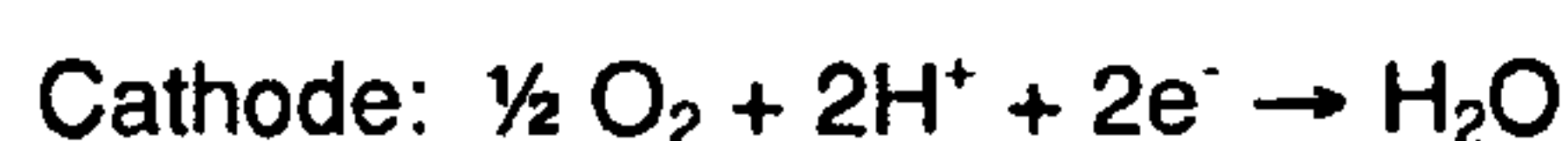
5 [0002] Fuel cells and electrochemical sensors for use in, for example, gas, smoke, and/or fire detectors have been known in the art for several years. See, for example, U.S. Patent No. 4,329,214 entitled "Gas Detection Unit," U.S. Patent No. 5,302,274 entitled "Electrochemical Gas Sensor Cells Using Three Dimensional Sensing Electrodes," U.S. Patent No. 5,331,310 entitled "Amperometric Carbon Monoxide Sensor
10 Module for Residential Alarms," U.S. Patent No. 5,573,648 entitled "Gas Sensor Based on Protonic Conductive Membranes," U.S. Patent No. 5,618,493 entitled "Photon Absorbing Bioderived Organometallic Carbon Monoxide Sensors," U.S. Patent No. 5,650,054 entitled "Low Cost Room Temperature Electrochemical Carbon Monoxide and Toxic Gas Sensor with Humidity Compensation Based on Protonic Conductive
15 Membranes," U.S. Patent No. 5,944,969 entitled "Electrochemical Sensor With A Non-Aqueous Electrolyte System," U.S. Patent No. 5,958,200 entitled "Electrochemical Gas Sensor," U.S. Patent No. 6,172,759 entitled "Target Gas Detection System with Rapidly Regenerating Optically Responding Sensors," U.S. Patent No. 6,200,443 entitled "Gas Sensor with a Diagnostic Device," U.S. Patent No. 6,936,147 entitled "Hybrid Film Type
20 Sensor," U.S. Patent No. 6,948,352 entitled "Self-Calibrating Carbon Monoxide Detector and Method," U.S. Patent No. 7,077,938 entitled "Electrochemical Gas Sensor," U.S. Patent No. 7,022,213 entitled "Gas Sensor and Its Method of Manufacture," U.S. Patent No. 7,236,095 entitled "Solid State Sensor for Carbon Monoxide," U.S. Patent No. 7,279,081 entitled "Electrochemical Sensor," U.S. Patent Publication No. 2005/0145494

entitled "Liquid Electrochemical Gas Sensor," U.S. Patent Publication No. 2006/0091007
 entitled "Gas Detecting Device with Self-Diagnosis for Electrochemical Gas Sensor,"
 U.S. Patent Publication No. 2006/0120924 entitled "Proton Conductor Gas Sensor," and
 U.S. Patent Publication No. 2006/0196770 entitled "Liquid Electrochemical Gas Sensor."

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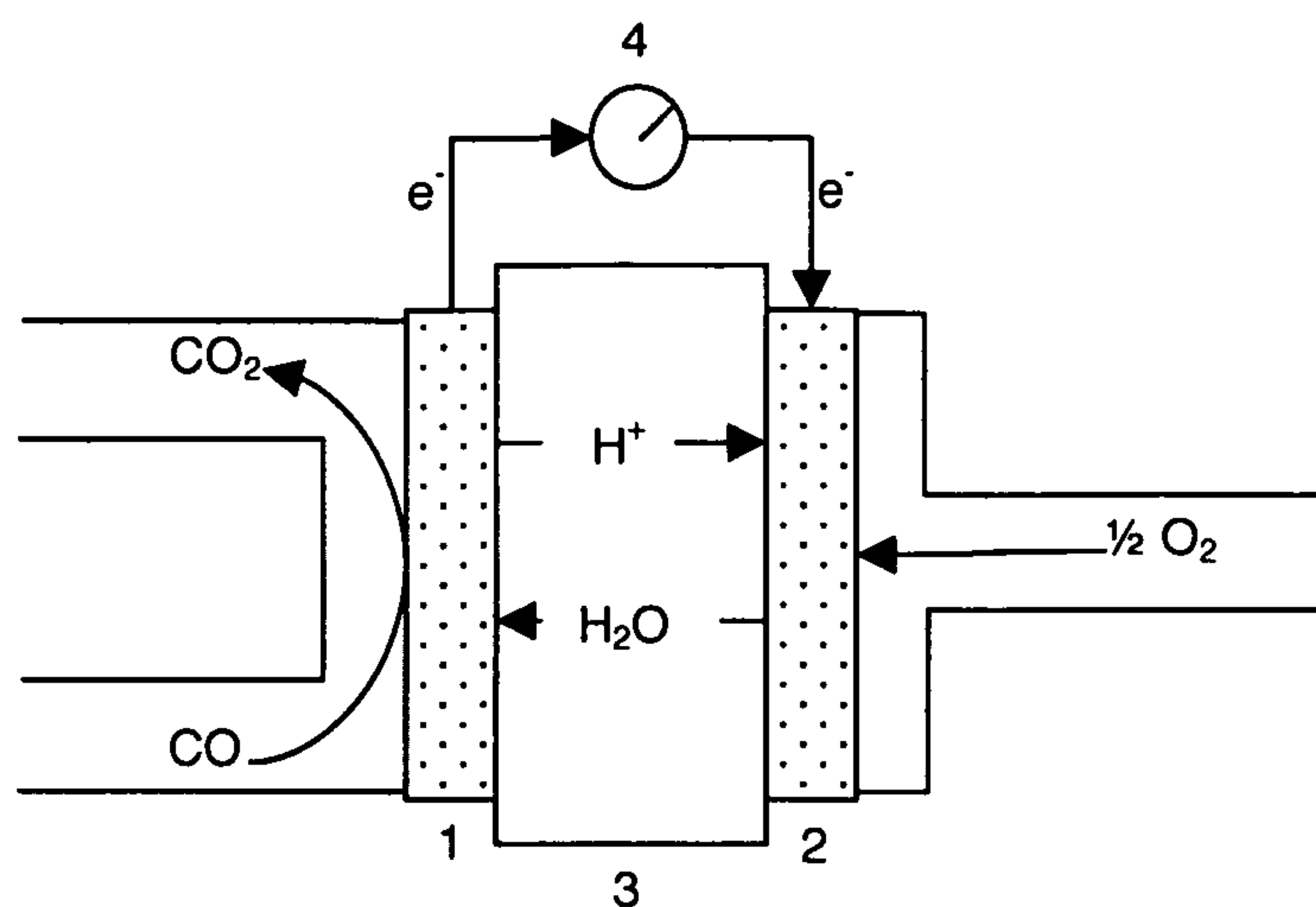
[0003] While the utilization of fuel cells and electrochemical sensors for use in
 gas, smoke, and/or fire detectors has become increasingly popular, sensor performance,
 cost, longevity, and/or configuration remains largely problematic.

10 [0004] Indeed, modern fuel cells and electrochemical sensors commonly use
 carbon supported noble metal catalysts, such as platinum at both the anode and the
 cathode. At the anode, platinum typically catalyses the oxidation of the fuel, such as
 hydrogen, methanol, carbon monoxide, etcetera. At the cathode, platinum typically
 catalyses the reduction of oxygen. For example, the chemical reactions that typically
 15 occur in an electrochemical carbon monoxide sensor are provided below:



[0005] As is shown below, due to the identical nature of the catalyst electrodes,
 20 without biasing the electrodes, electric current generation (e^-) can typically only occur if
 both the anode and the cathode are separated and sealed from each other to prevent
 gas crossover. The two electrodes are typically separated by a membrane that allows for
 diffusion of ions, such as protons (H^+), and water (H_2O). Gas crossover through the
 membrane is possible, but the diffusion rate of the sample gas is controlled so that the

fuel gas (H_2 , CO , etcetera) is effectively scrubbed from the sample gas by the anode and only oxygen is allowed to crossover to the cathode.



1. Anode
2. Cathode
3. Ion Exchange Membrane
4. Sensing Circuit

Prior Art Micro Electrode Assembly

5 [0006] When both the anode and the cathode comprise identical materials, in this case carbon supported platinum, there can be several problems. The first occurs when the gas diffusion is not controlled and the gases crossover from one electrode to the other. This can lead to degradation of the electrodes through peroxide formation or oxidation. In an electrochemical sensor, gas crossover results in reduced signal strength and polarization of the sensor which can potentially lead to sensor malfunction. Platinum is sensitive to poisoning from external contaminants, such as sulfur compounds, which reduces the electrical current being generated. Electrode sensitivity can also drop over time due to reduced surface area of the platinum particles caused by rearrangement and sintering. Additionally, amorphous carbon which is a common material used as a carbon

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support, (e.g., XC72 (Cabot Corporation) or Black Pearls (Cabot Corporation)) is susceptible to oxidation. The oxidation reaction can even be catalyzed by the very materials that the carbon is meant to support, such as Pt, Ru, Pd, etcetera. This oxidation can result in the presence of a background current in a sensor application, reduced electrical conductivity within the electrodes, and migration and aggregation of metal nanoparticles resulting in reduced power output or sensitivity. This is especially problematic for a sensor application in which long term drift and reduced sensitivity can be catastrophic. Finally, platinum is a noble metal that is rare and expensive.

[0007] It is therefore an object of the present invention, among other objects, to provide novel anodic and/or cathodic materials which replace conventional platinum based electrodes in fuel cells and electrochemical sensors. It is also an object of the present invention to provide novel device configurations which are enabled by the use of these novel materials for the anode and/or cathode.

[0008] These and other objects of the present invention will become apparent in light of the present specification, claims, and drawings.

SUMMARY OF THE INVENTION

[0009] The present invention is directed to a cathodic material for use in an electrochemical sensor comprising: a carbonaceous material and an oxygen reduction catalyst associated with the carbonaceous material, wherein the cathodic material does not materially exhibit catalytic activity for the oxidation of carbon monoxide. The carbonaceous material preferably acts as a support and/or an electron conductor. The cathodic material is also optionally associated with an ion-exchange material, such as proton conducting Nafion (Dupont), polystyrene sulfonic acid (Sigma-Aldrich), H₃PO₄ doped polybenzimidazole derivatives (L. Xiao, *et al.*, *Fuel Cells* 5 (2005) 287), protic

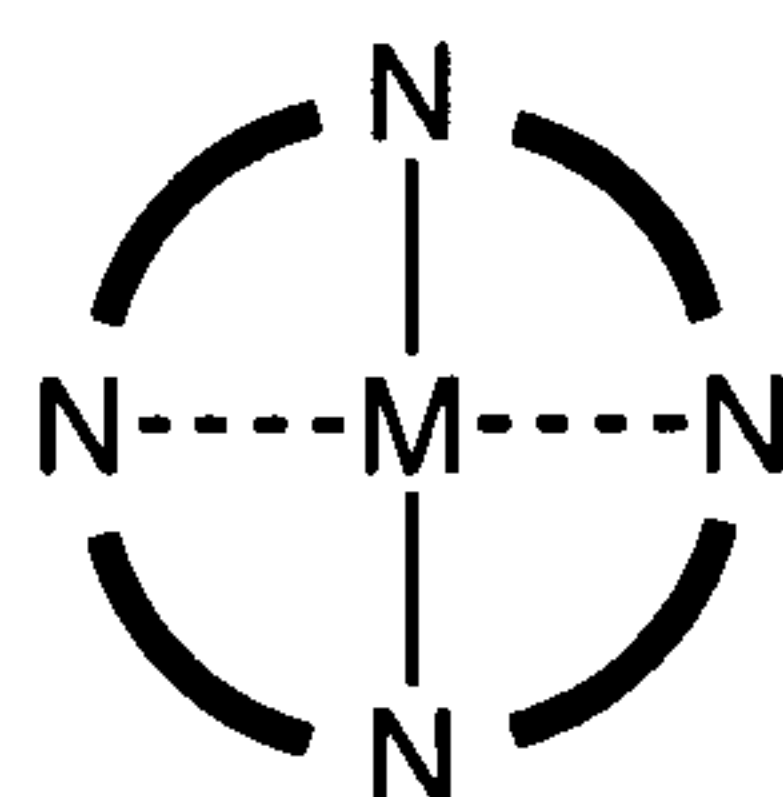
ionic liquid doped polybenzimidazole derivatives, and protic ionic liquid doped sulfonated polyimide derivatives (S.-Y. Lee, *et al.*, *J. Power Sources* (2009)), etcetera.

[0010] In a preferred embodiment of the present invention, the oxygen reduction catalyst comprises a material resulting from pyrolysis of at least one of the group comprising substituted transition metal (*i.e.*, d-block) porphyrins, unsubstituted transition metal porphyrins, substituted transition metal tetrabenzoporphyrins, unsubstituted transition metal tetrabenzoporphyrins, substituted transition metal tetraphenylporphyrins, unsubstituted transition metal tetraphenylporphyrins, substituted transition metal tetraazaporphyrins, unsubstituted transition metal tetraazaporphyrins, substituted transition metal tetraazamacrocycles, unsubstituted transition metal tetraazamacrocycles, substituted transition metal phthalocyanines, unsubstituted transition metal phthalocyanines, substituted transition metal naphthalocyanines, unsubstituted transition metal naphthalocyanines, substituted transition metal bis(phthalocyanines), unsubstituted transition metal bis(phthalocyanines), substituted transition metal bis(naphthalocyanines), unsubstituted transition metal bis(naphthalocyanines), and/or combinations thereof.

[0011] In another preferred embodiment of the present invention, the oxygen reduction catalyst comprises a material resulting from pyrolysis of at least one of the group comprising substituted cobalt porphyrins, unsubstituted cobalt porphyrins, substituted cobalt tetrabenzoporphyrins, unsubstituted cobalt tetrabenzoporphyrins, substituted cobalt tetraphenylporphyrins, unsubstituted cobalt tetraphenylporphyrins, substituted cobalt tetraazaporphyrins, unsubstituted cobalt tetraazaporphyrins, substituted cobalt tetraazamacrocycles, unsubstituted cobalt tetraazamacrocycles, substituted cobalt metal phthalocyanines, unsubstituted cobalt phthalocyanines,

substituted cobalt naphthalocyanines, unsubstituted cobalt naphthalocyanines, substituted cobalt bis(phthalocyanines), unsubstituted cobalt bis(phthalocyanines), substituted cobalt bis(naphthalocyanines), unsubstituted cobalt bis(naphthalocyanines), and/or combinations thereof.

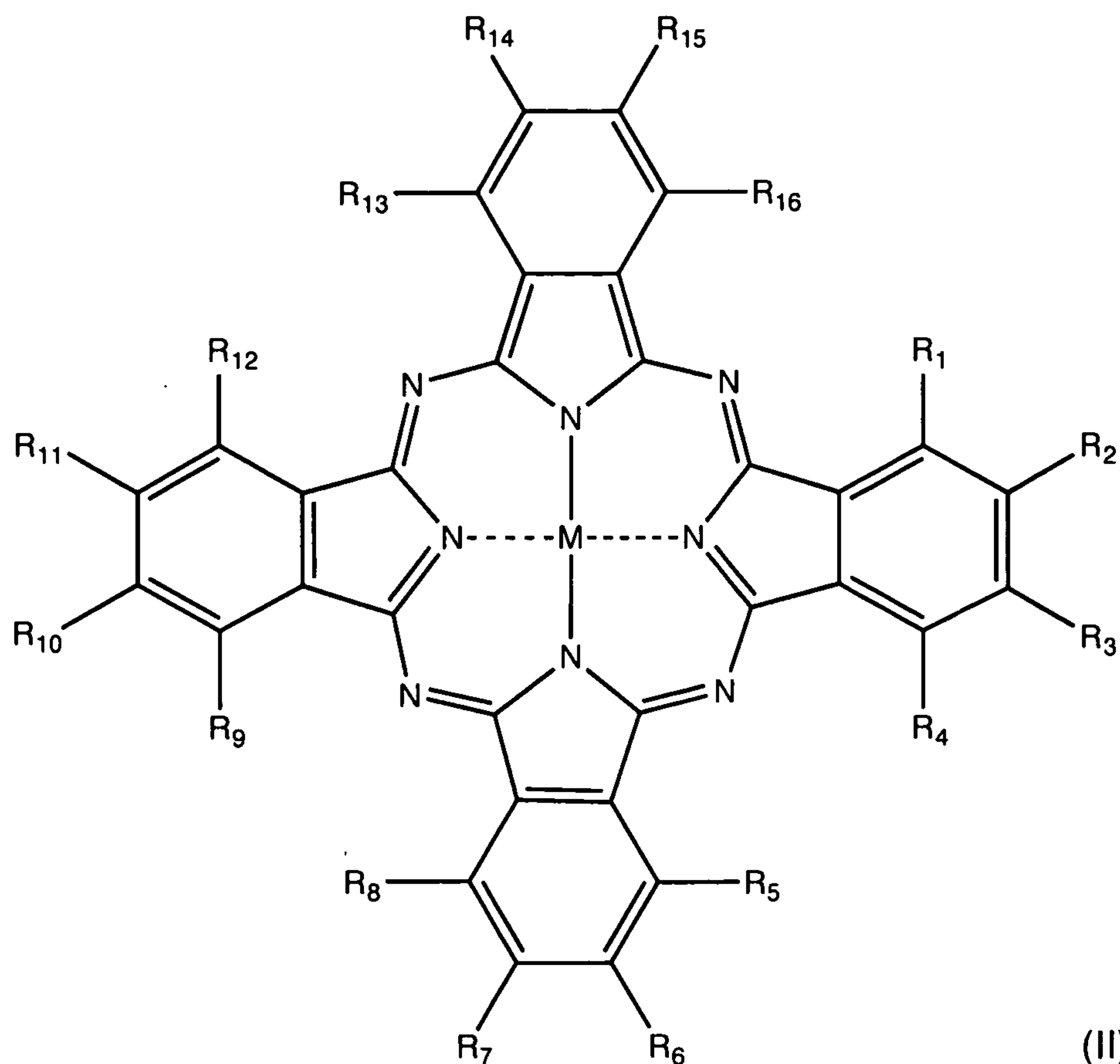
5 [0012] In yet another preferred embodiment of the present invention, the oxygen reduction catalyst comprises a material resulting from pyrolysis of at least one of a compound, a structural isomer of a compound, and mixtures of isomers of compounds, represented by the following structure:



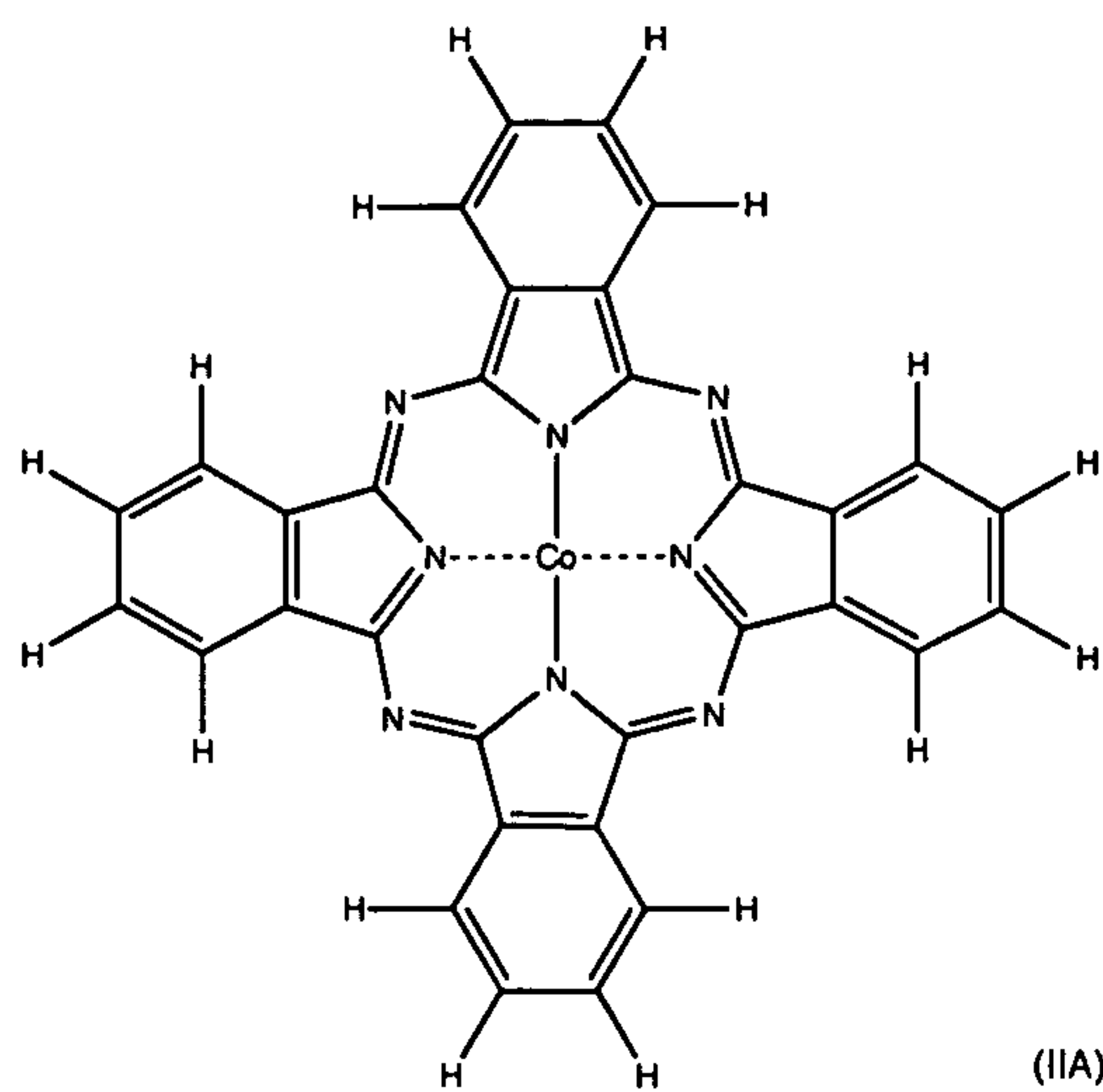
(I)

10 wherein M comprises a transition metal ligated by a tetraazamacrocycle, including, but not limited to, substituted porphyrins, unsubstituted porphyrins, substituted phthalocyanines, unsubstituted phthalocyanines, substituted naphthalocyanines, unsubstituted naphthalocyanines, and combinations thereof – just to name a few.

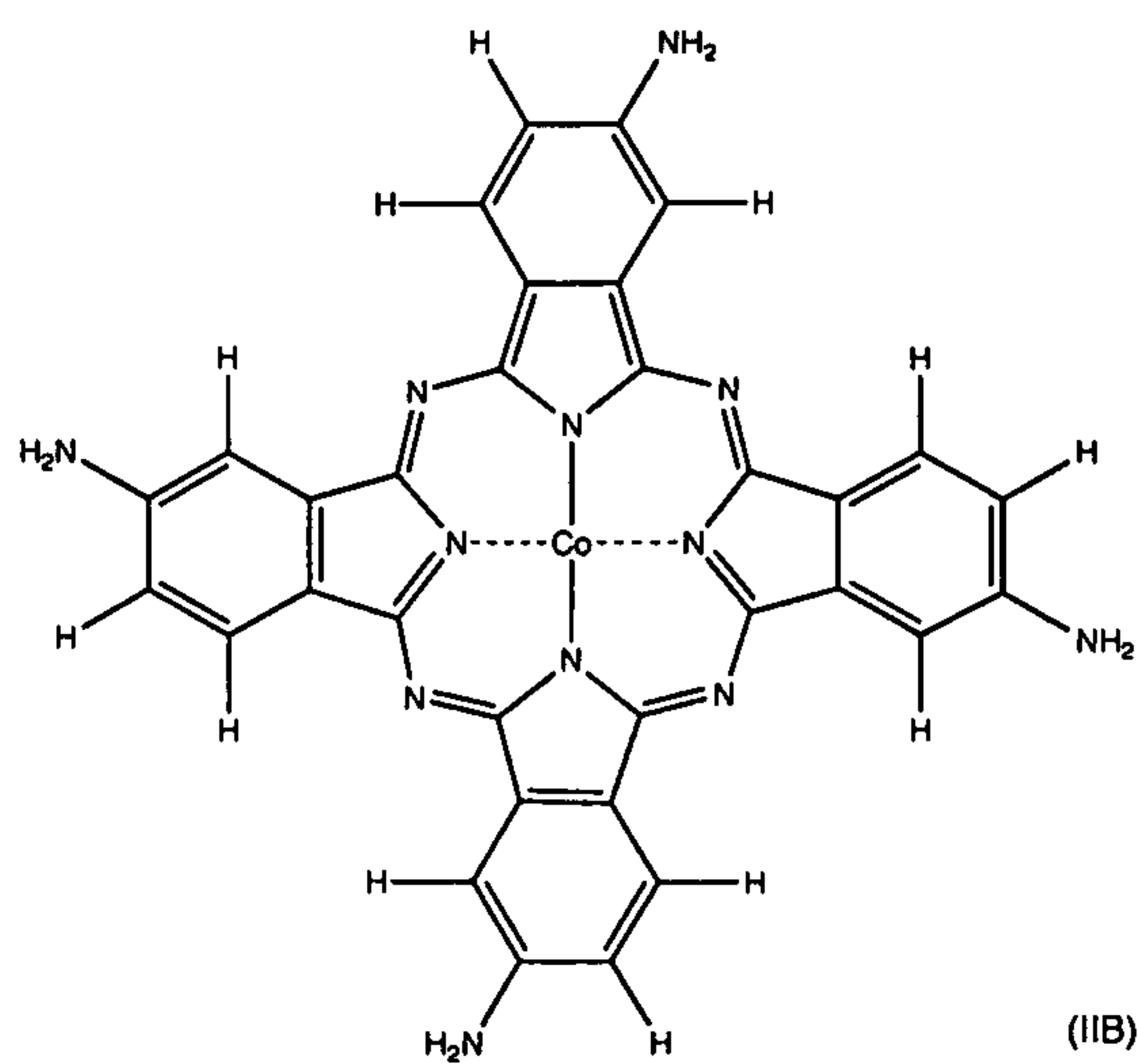
[0013] In one embodiment of the present invention, the oxygen reduction catalyst
15 comprises a material resulting from pyrolysis of at least one of a compound, a structural isomer of a compound, and mixtures of isomers of compounds, represented by the following formula:



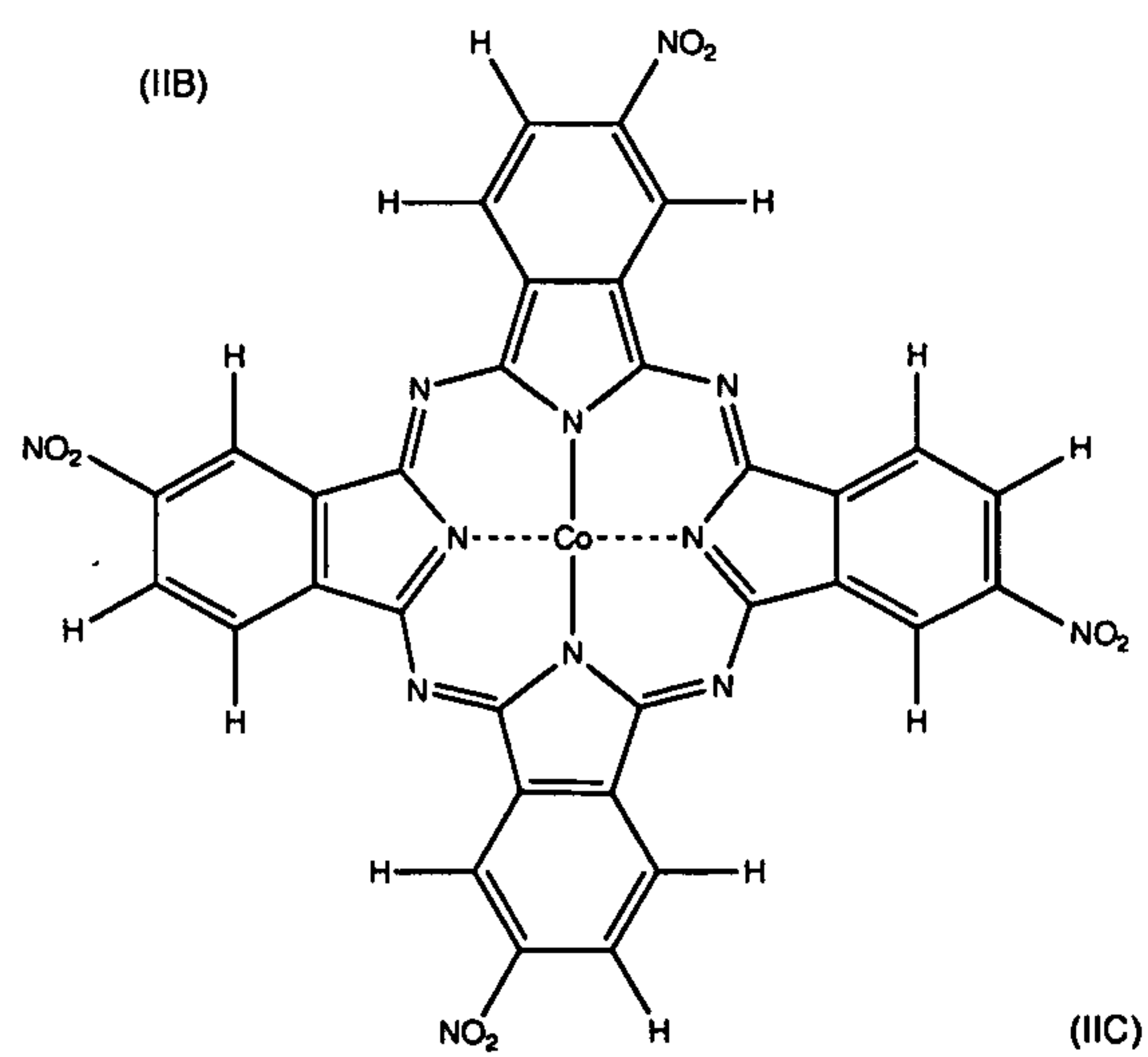
wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{16} are the same or different and comprise H, NO_2 , NH_2 , NHR_{17} , $\text{N}(\text{R}_{18})_2$, CO_2H , CO_2R_{19} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{20} , SH , SR_{21} , and combinations thereof; and wherein R_{17-21} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s). In this embodiment, the oxygen reduction catalyst preferably comprises a material resulting from pyrolysis of one or more of a compound, a structural isomer of a compound, and mixtures of isomers of compounds, represented by the following formulae:



(IIA)

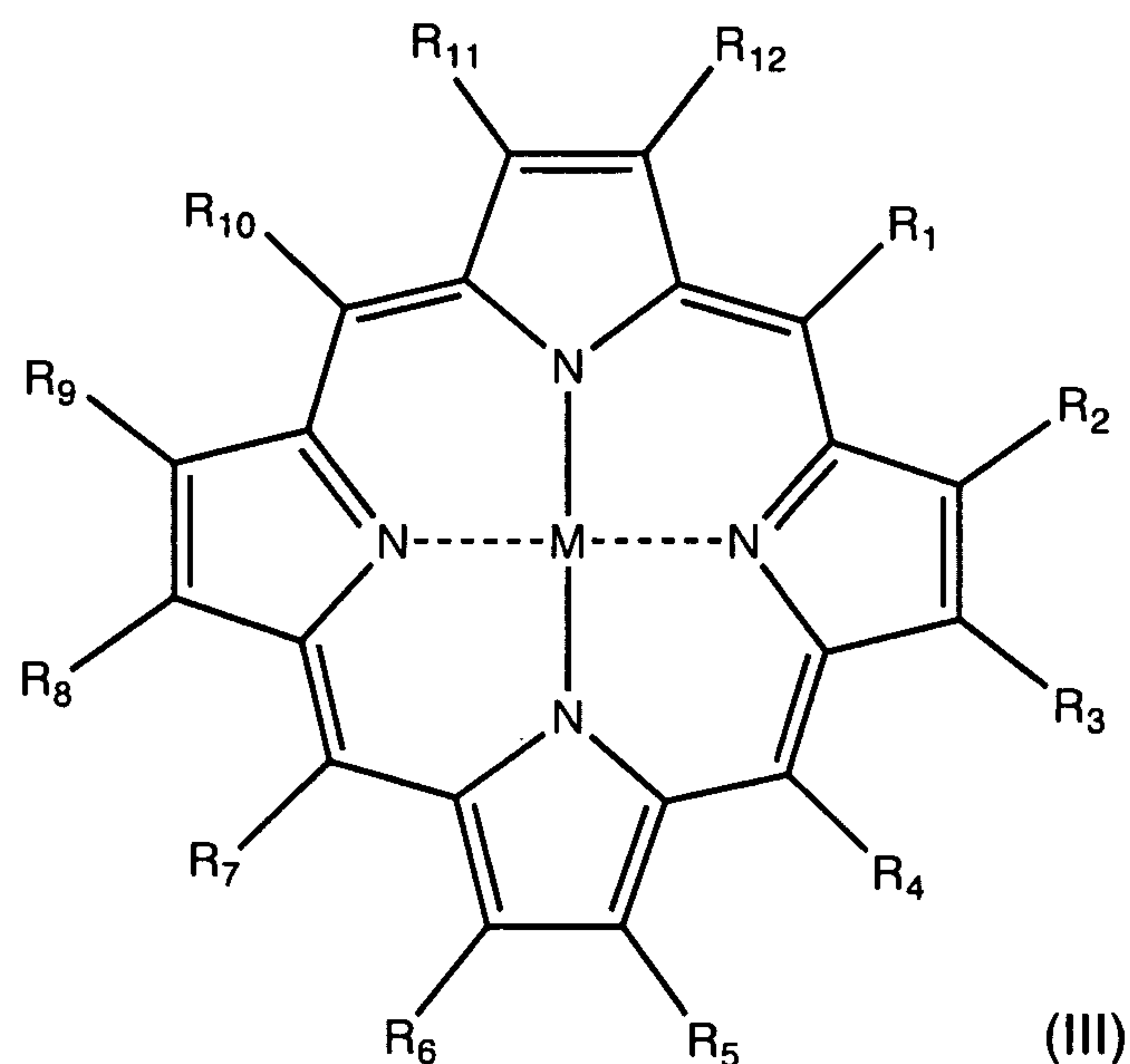


(IIB)



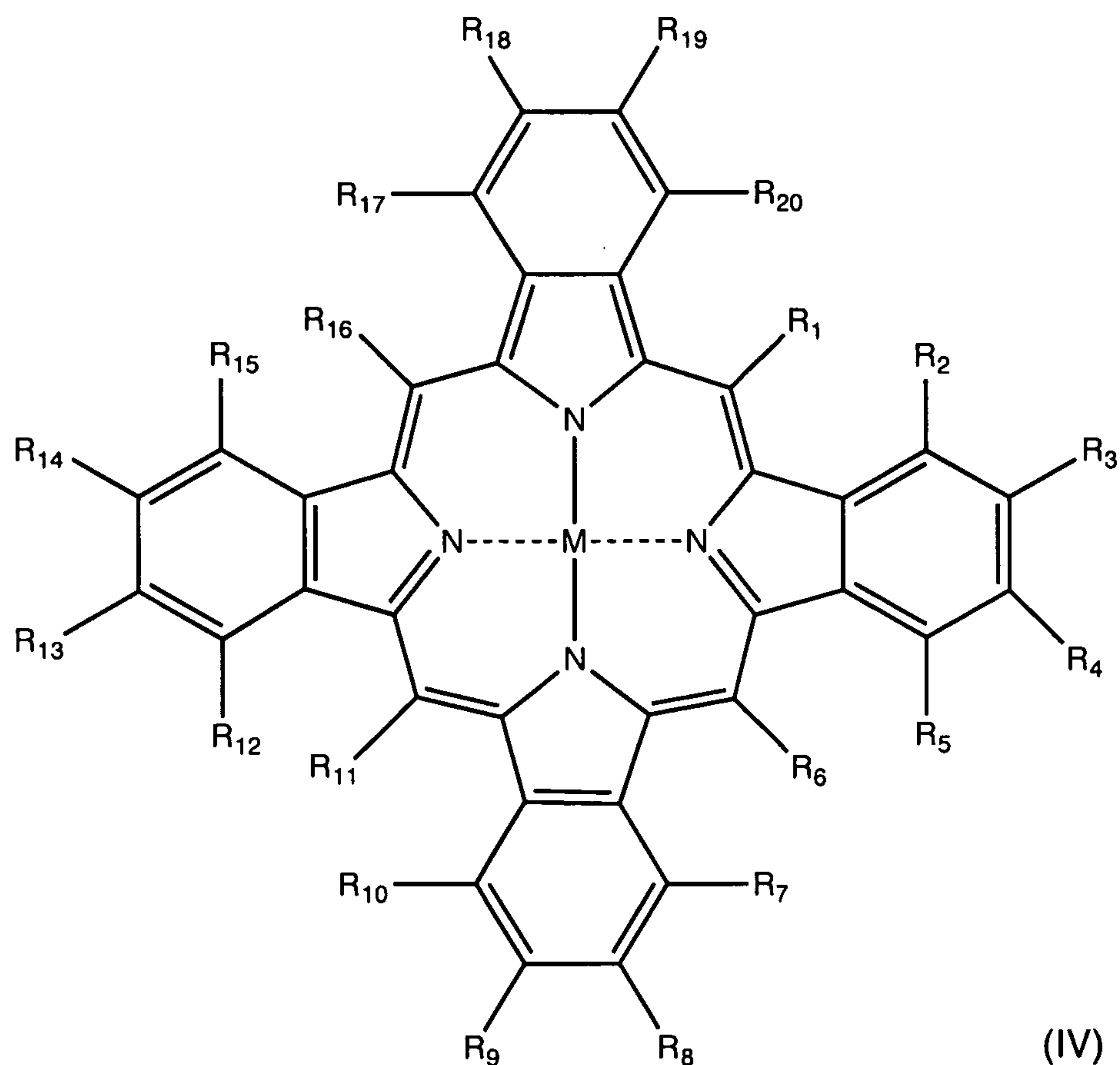
(IIC)

[0014] In a preferred embodiment of the present invention, the oxygen reduction catalyst comprises a material resulting from pyrolysis of at least one of a compound, a structural isomer of a compound, and mixtures of isomers of compounds, represented by the following formula:



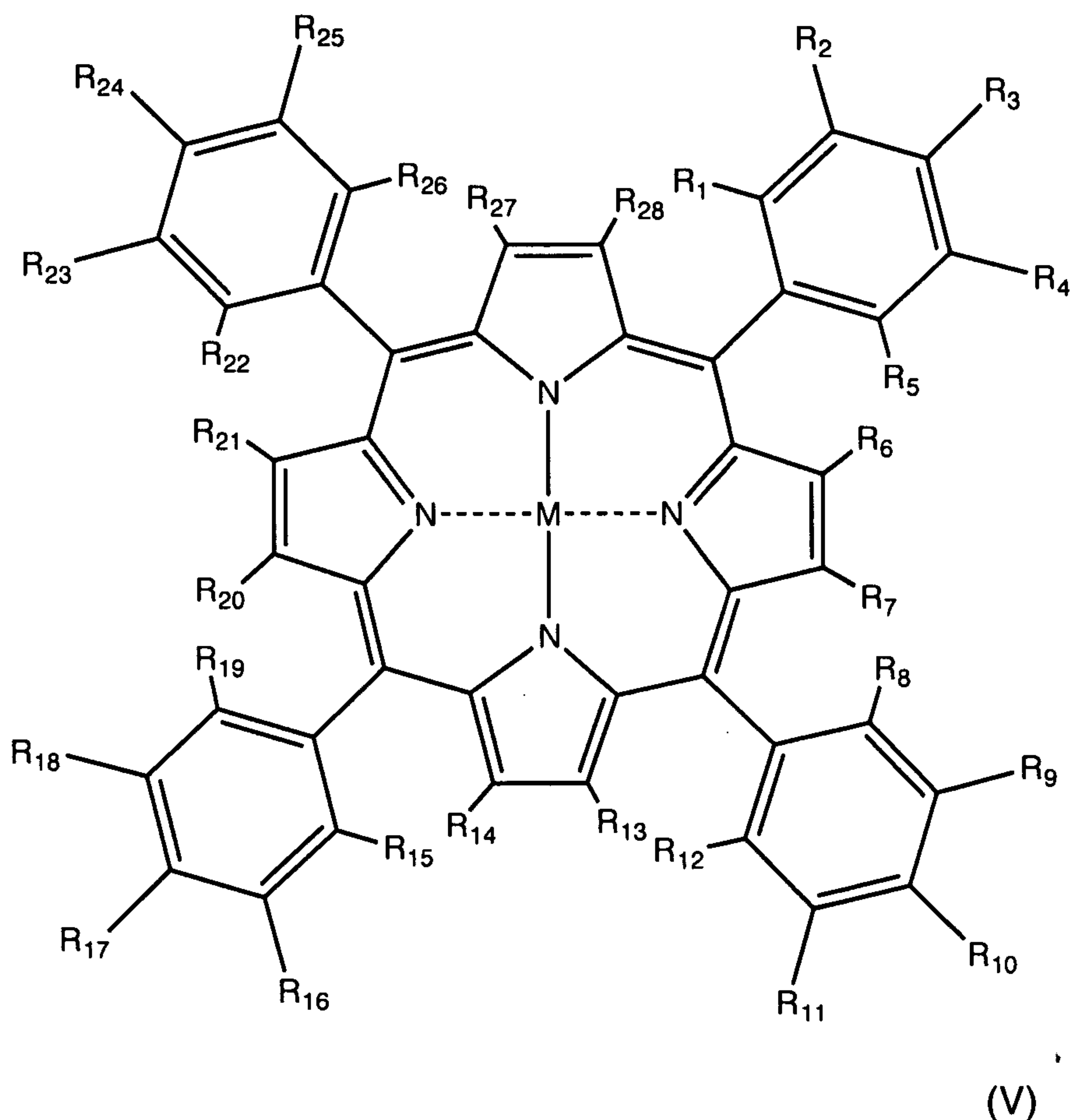
wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{12} are the same or different and comprise H, NO_2 , NH_2 , NHR_{13} , $\text{N}(\text{R}_{14})_2$, CO_2H , CO_2R_{15} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{16} , SH , SR_{17} , and combinations thereof; and wherein R_{13-17} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s).

[0015] In another preferred embodiment of the present invention, the oxygen reduction catalyst comprises a material resulting from pyrolysis of at least one of a compound, a structural isomer of a compound, and mixtures of isomers of compounds, represented by the following formula:



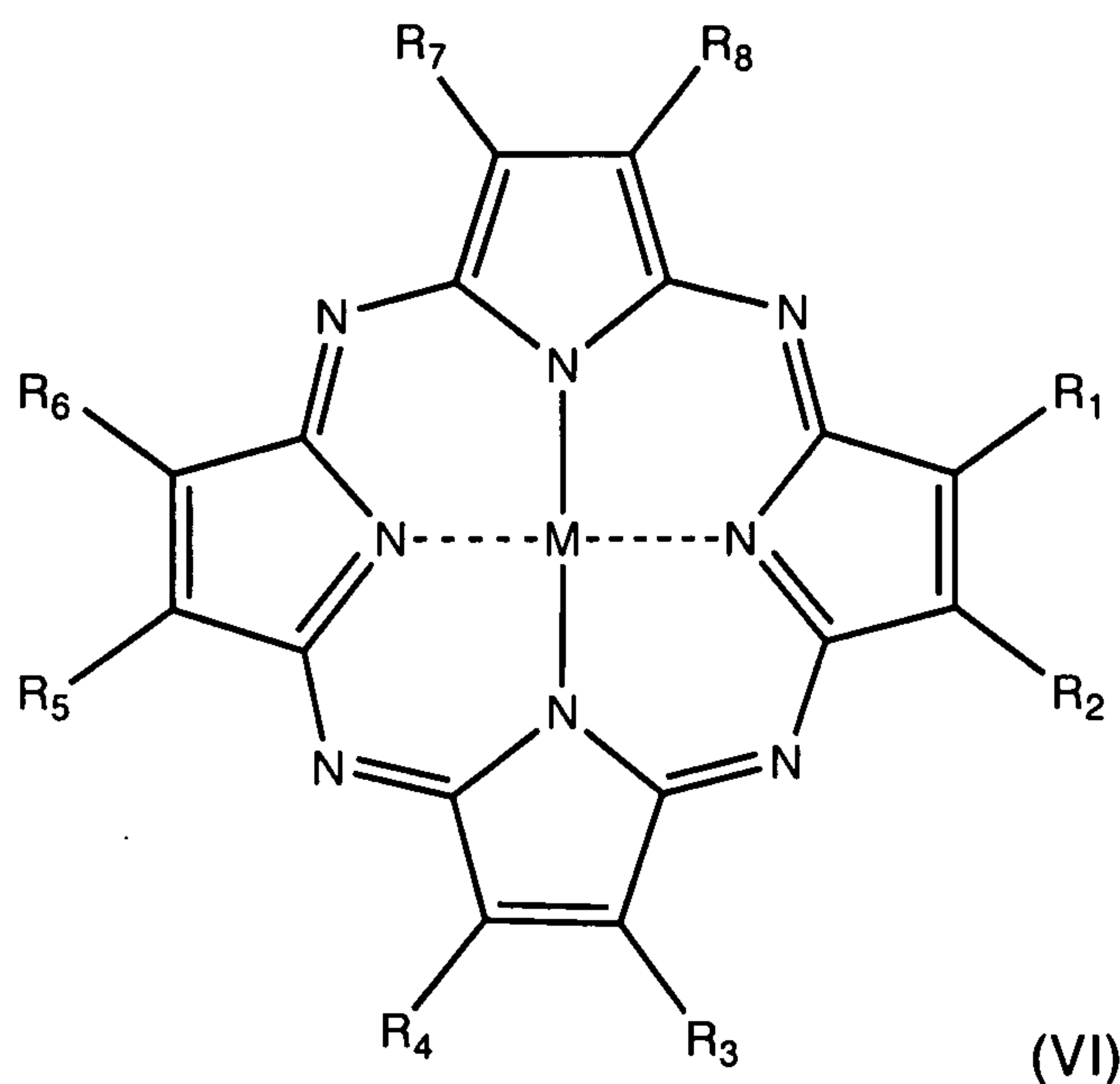
wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{20} are the same or different and comprise H, NO_2 , NH_2 , NHR_{21} , $\text{N(R}_{22})_2$, CO_2H , CO_2R_{23} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{24} , SH , SR_{25} , and combinations thereof; and wherein R_{21-25} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s).

[0016] In yet another preferred embodiment of the present invention, the oxygen reduction catalyst comprises a material resulting from pyrolysis of at least one of a compound, a structural isomer of a compound, and mixtures of isomers of compounds, represented by the following formula:



wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{28} are the same or different and comprise H, NO_2 , NH_2 , NHR_{29} , $\text{N(R}_{30})_2$, CO_2H , CO_2R_{31} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{32} , SH , SR_{33} , and combinations thereof; and wherein R_{29-33} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s).

[0017] In one aspect of an embodiment of the present invention, the oxygen reduction catalyst comprises a material resulting from pyrolysis of at least one of a compound, a structural isomer of a compound, and mixtures of isomers of compounds, represented by the following formula:



wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R₁-R₈ are the same or different and comprise H, NO₂, NH₂, NHR₉, N(R₁₀)₂, CO₂H, CO₂R₁₁, an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR₁₂, SH, SR₁₃, and combinations thereof; and wherein R₉₋₁₃ are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s).

[0018] Preferably, the carbonaceous materials associated with the present invention comprise, for example, graphene, graphite, amorphous carbon, carbon nanotubes, carbon fibers, and combinations thereof. The carbon nanotubes include, for example, single walled nanotubes (SWNT), double walled nanotubes (DWNT), and multi-walled nanotubes (MWNT), all of which may optionally be doped with atoms such as, but not limited to, nitrogen, boron, and/or phosphorous.

[0019] The present invention is also directed to an electrochemical sensor for use in a gas detector comprising: a housing, wherein the housing is capable of containing a micro electrode assembly therein (*e.g.*, one or more side walls, and a bottom wall cooperatively define a containment region for containing the micro electrode assembly), and further wherein the housing comprises a gaseous diffusion aperture; and a micro electrode assembly which comprises an anode, a cathode comprising one or more cathodic materials as are disclosed herein, and an ion exchange membrane, wherein the ion exchange membrane permits ion transport (*e.g.*, hydrogen ions (protons), hydroxide ions, carbonate ions, etcetera) between the anode and the cathode, and further wherein the ion exchange membrane prevents electron conduction between the anode and the cathode. The electrochemical sensor may also include a desiccant for retaining a liquid, such as water and/or a reservoir. The electrochemical sensor may further comprise a configuration to prevent water from freezing, such as antifreeze or salts. The electrochemical sensor may additionally comprise a configuration that is at least substantially waterless (See Figure 1B).

[0020] In a preferred embodiment of the present invention, the anode and the cathode of the micro electrode assembly are disposed upon opposite sides of the ion exchange membrane and/or exposed to a different gaseous environment (*e.g.*, a first configuration). Alternatively, the anode and the cathode of the micro electrode assembly are disposed upon the same side of the ion exchange membrane and/or exposed to the same gaseous environment (*e.g.*, a second configuration).

[0021] The present invention is further directed to an electrochemical sensor for use in a gas detector comprising: a housing, wherein the housing is capable of containing a micro electrode assembly therein (*e.g.*, one or more side walls, and a

bottom wall cooperatively define a containment region for containing the micro electrode assembly), and further wherein the housing comprises a gaseous diffusion aperture; and a micro electrode assembly which comprises an anode, a cathode, and an ion exchange membrane, wherein the anode and the cathode are disposed upon the same side of the ion exchange membrane and/or exposed to the same gaseous environment.

[0022] These and other features, advantages, and objects of the present invention will be further understood and appreciated by those skilled in the art by reference to the following specification, claims, and appended drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] Certain embodiments of the present invention are illustrated by the accompanying figures. It will be understood that the figures are not necessarily to scale and that details not necessary for an understanding of the invention or that render other details difficult to perceive may be omitted. It will be further understood that the invention is not necessarily limited to the particular embodiments illustrated herein.

[0024] The invention will now be described with reference to the drawings wherein:

[0025] Figure 1A of the drawings is a cross-sectional schematic representation of an electrochemical sensor fabricated in accordance with the present invention, showing among other things, a solvent reservoir;

[0026] Figure 1B of the drawings is a cross-sectional schematic representation of a solventless (*e.g.*, waterless) electrochemical sensor fabricated in accordance with the present invention;

[0027] Figure 1C of the drawings is a cross-sectional schematic representation of an electrochemical sensor fabricated in accordance with the present invention,

showing among other things, a top/cover filter;

[0028] Figures 2A-2B of the drawings are perspective and exploded perspective representations, respectively, of micro electrode assemblies fabricated in accordance with the present invention;

5 [0029] Figures 3A-3D of the drawings are representations of micro electrode assemblies fabricated in accordance with the present invention;

[0030] Figures 4A-4D of the drawings are representations of micro electrode assemblies associated with reference electrodes fabricated in accordance with the present invention;

10 [0031] Figure 5 of the drawings is a representation of a micro electrode assembly having a key member fabricated in accordance with the present invention;

[0032] Figure 6 of the drawings is a cyclic voltammagram verifying that embodiments of the present invention are electrochemically active towards the reduction of oxygen;

15 [0033] Figure 7 of the drawings is a cyclic voltammagram verifying that oxygen reduction catalysts of the present invention are materially electrochemically inactive with regard to the oxidation of carbon monoxide and the reduction of carbon dioxide;

[0034] Figure 8A-8B of the drawings are two-dimensional plots showing sensor performance output as a function of exposure time to pulsed CO and;

20 [0035] Figure 9 of the drawings is a two-dimensional plot showing a linear response of a sensor fabricated in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0036] Referring now to the drawings and to Figure 1A in particular, a cross-sectional schematic representation of electrochemical (EC) sensor 10 is shown, which generally comprises housing 12 and micro electrode assembly (MEA) 14.

5 [0037] It will be understood that electrochemical sensor 10 may comprise, for illustrative purposes only, an electrochemical gas sensor for a gas, smoke, and/or fire detector, and the like. It will be further understood that Figure 1A is merely a schematic representation of electrochemical sensor 10. As such, some of the components may have been distorted from their actual scale for pictorial clarity. Indeed, numerous other
10 electrochemical cell designs and configurations are contemplated for use, including those disclosed in U.S. Patent No. 4,329,214 entitled "Gas Detection Unit," U.S. Patent No. 5,302,274 entitled "Electrochemical Gas Sensor Cells Using Three Dimensional Sensing Electrodes," U.S. Patent No. 5,331,310 entitled "Amperometric Carbon Monoxide Sensor Module for Residential Alarms," U.S. Patent No. 5,573,648 entitled
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Carbon Monoxide Detector and Method," U.S. Patent No. 7,077,938 entitled
"Electrochemical Gas Sensor," U.S. Patent No. 7,022,213 entitled "Gas Sensor and Its
Method of Manufacture," U.S. Patent No. 7,236,095 entitled "Solid State Sensor for
Carbon Monoxide," U.S. Patent No. 7,279,081 entitled "Electrochemical Sensor," U.S.
5 Patent Publication No. 2005/0145494 entitled "Liquid Electrochemical Gas Sensor," U.S.
Patent Publication No. 2006/0091007 entitled "Gas Detecting Device with Self-Diagnosis
for Electrochemical Gas Sensor," U.S. Patent Publication No. 2006/0120924 entitled
"Proton Conductor Gas Sensor," and U.S. Patent Publication No. 2006/0196770 entitled
"Liquid Electrochemical Gas Sensor,"

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[0038] In accordance with the present invention housing 12 is capable of
containing a micro electrode assembly therein, and preferably includes first side wall 16,
second side wall 18, and bottom wall 20, which define containment region 23 for
containing micro electrode assembly 14 therein, among other sub-components. Housing
12 also preferably includes top wall 22 having gaseous diffusion aperture 24 which
15 allows gasses external to electrochemical sensor 10 to electrochemically interact with
micro electrode assembly 14. It will be understood that while housing 12 has been
disclosed, for illustrative purposes only, as comprising top wall 22, gaseous diffusion
aperture 24 may emanate from first side wall 16 to second sidewall 18, thereby
20 minimizing or eliminating the structural necessity of top wall 22. It will be further
understood that top wall 22 may be fabricated from a material different than first side wall
16 and/or second side wall 18, thereby forming a separate and distinct housing cap. As
is known in the art, housing 12 may also include filter 32, such as particulate filter and/or
activated carbon filter, which enhances the longevity and electrochemical performance of

micro electrode assembly 14. In addition housing 12 may optionally include reservoir region 34 which contains/retains solvents/fluids, such as water and/or electrochemical cell redox agents. In a preferred embodiment of the present invention, reservoir region 34 may include a desiccant gel for retaining water or other agents that influence the chemical and/or physical properties of water. Housing 12 also preferably includes electrode leads 36, which enable electrical communication with a sensing circuit.

[0039] As is best shown in Figure 1B, electrochemical sensor 10 may be solventless (e.g., waterless) and void of reservoir region 34. In this embodiment electrochemical sensor 10 may optionally comprise an ion exchange member which preferably comprises H_3PO_4 doped polybenzimidazole derivatives, protic ionic liquid doped polybenzimidazole derivatives, and/or protic ionic liquid doped sulfonated polyimide derivatives, which are ionically conductive regardless of the level of ambient humidity/moisture

[0040] As is best shown in Figure 1C, electrochemical sensor 10 may further comprise a top or cover filter 50 which covers gaseous diffusion aperture 24 (*i.e.*, the sample gas inlet) and removes unwanted contaminant gases from the sample gas that the sensor may be cross-sensitive to. Additionally cover filter 50 enables the sensor to be washed. Cover filter 50 may comprise an ePTFE (expanded Teflon such as Gore-Tex), a charcoal impregnated felt (Calgon Carbon, Pittsburgh, PA), and/or a housing filled with activated charcoal powder or pellets (Calgon Carbon, Pittsburgh, PA; Norit Americas Inc., Marshall, TX).

[0041] For purposes of the present disclosure, housing 12 may be fabricated from one or more of any one of a number of materials including, for example, metals, metallic alloys, pseudo metals, natural and/or synthetic plastics, and composites – just to

name a few.

[0042] Referring now to Figures 1A-1C and 2A-2B, collectively, micro electrode assembly 14 preferably includes anode 26, cathode 28, ion exchange membrane 30, and outer substrate(s) 38 (*e.g.*, a porous Teflon diffusion layer). Individual current collectors 25 are preferably associated with anode 26 and cathode 28, and comprise, for example, carbonaceous conductors such as carbon based conductive paints (XCMC-40, Spraylat Corporation) or conductive carbon loaded silicone rubber (SE65 Conductive Silicone, Stockwell Elastomerics, Inc.) and/or metallic conductors. It will be understood that ion exchange membrane or material 30 generally permits hydrogen or other ion transport between anode 26 and cathode 28, but generally prevents electron conduction between the same. Non-limiting examples of suitable ion exchange membrane materials include, for example, expanded PTFE (Gore, Porex), glass wool, and/or cellulose which may be infused with various ion conducting materials such as mineral acids including H₂SO₄, aqueous alkaline salts such as KOH, H₃PO₄ doped polybenzimidazole derivatives (L. Xiao, *et al.*, *Fuel Cells* 5 (2005) 287), protic ionic liquid doped polybenzimidazole derivatives, and protic ionic liquid doped sulfonated polyimide derivatives (S.-Y. Lee, *et al.*, *J. Power Sources* (2009)). Other suitable ion exchange membrane materials include solid polymeric electrolytes 20 including, but not limited to, polystyrene sulfonic acid (Sigma-Aldrich) Nafion (Dupont), and/or Flemion (Asahi).

[0043] Anode 26 preferably serves as a working or sensing gaseous oxidation electrode, such as a carbon monoxide oxidation electrode which was discussed *supra* (See for example, ¶ 0004, and Figure 1A). Anode 26 may be fabricated from any one of

a number of materials including transition metals, alloys, and mixtures of the same. For example, platinum and platinum-ruthenium which can be associated with a carbonaceous species, such as graphene, graphite, amorphous carbon (XC72, BlackPearls), carbon nanotubes (*e.g.*, SWNT, DWNT, MWNT), carbon fibers, and combinations thereof, all of which may be doped with atoms such as, but not limited to, nitrogen, boron, and/or phosphorous – utilizing conventional techniques. Anode 26 may also be associated with an ion conductor, such as Nafion in an analogous manner disclosed *infra* with regard to the working examples of cathode 28. Additional suitable anodic materials include those disclosed in FUEL CELL FUNDAMENTALS, 2nd Ed., O'hayre et al., Wiley (2009).

[0044] Preferably cathode 28 comprises a cathodic material which includes a carbonaceous material, such as graphene, graphite, amorphous carbon, carbon nanotubes (*e.g.*, SWNT, DWNT, MWNT), carbon fibers, and combinations thereof, all of which may be doped with atoms such as, but not limited to, nitrogen, boron, and/or phosphorous – utilizing conventional techniques, and an oxygen reduction catalyst associated (*i.e.*, chemically and/or physically) with the carbonaceous material. It will be understood that the oxygen reduction catalysts of the present invention are preferably heat treated, pyrolyzed, and/or otherwise activated in a manner which enable the catalysts to remain functionally operable and stable. Notably, the cathodic materials of the present invention preferably do not materially exhibit catalytic activity for the oxidation of carbon monoxide and/or the reduction of carbon dioxide. Cathode 28 may also be associated with an ion conductor, such as Nafion, in an analogous manner disclosed *infra* with regard to the working examples of the cathode. Such

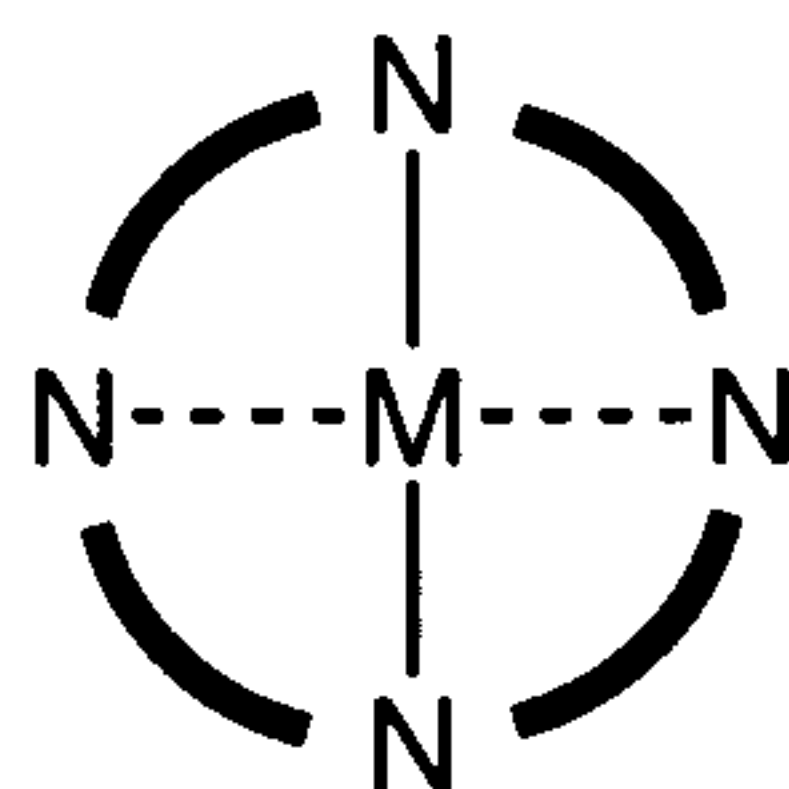
electrochemically selective catalysts enables traditional MEA configurations (e.g., wherein the anode and the cathode of the micro electrode assembly are disposed upon opposite sides of the ion exchange membrane and/or exposed to different gaseous environments (See diagram between ¶¶ 0005-0006), as well as novel electrode configurations wherein the anode and the cathode of the micro electrode assembly are disposed upon the same side of the ion exchange membrane and/or exposed to the same gaseous environment (See Figures 1-5).

[0045] In accordance with one embodiment of the present invention, cathode 28 preferably serves as a counter electrode in the MEA and participates in the catalyzed reduction of oxygen to water which was discussed *supra* (See ¶ 0004).

[0046] Non-limiting examples of suitable oxygen reduction catalysts include a material resulting from pyrolysis of substituted, transition metal (*i.e.*, d-block) porphyrins, unsubstituted transition metal porphyrins, substituted transition metal tetrabenzoporphyrins, unsubstituted transition metal tetrabenzoporphyrins, substituted transition metal tetraphenylporphyrins, unsubstituted transition metal tetraphenylporphyrins, substituted transition metal tetraazaporphyrins, unsubstituted transition metal tetraazaporphyrins, substituted transition metal tetraazamacrocycles, unsubstituted transition metal tetraazamacrocycles, substituted transition metal phthalocyanines, unsubstituted transition metal phthalocyanines, substituted transition metal naphthalocyanines, unsubstituted transition metal naphthalocyanines, substituted transition metal bis(phthalocyanines), unsubstituted transition metal bis(phthalocyanines), substituted transition metal bis(naphthalocyanines), unsubstituted transition metal bis(naphthalocyanines), and/or combinations thereof. Examples of preferred transition metals include, but are not limited to, Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru,

or Zn, with Co being the most preferred transition metal.

[0047] Suitable oxygen reduction catalysts may also be expressed as comprising a material resulting from pyrolysis of a compound, a structural isomer of a compound, and/or mixtures of isomers of compounds, represented by the following structure:

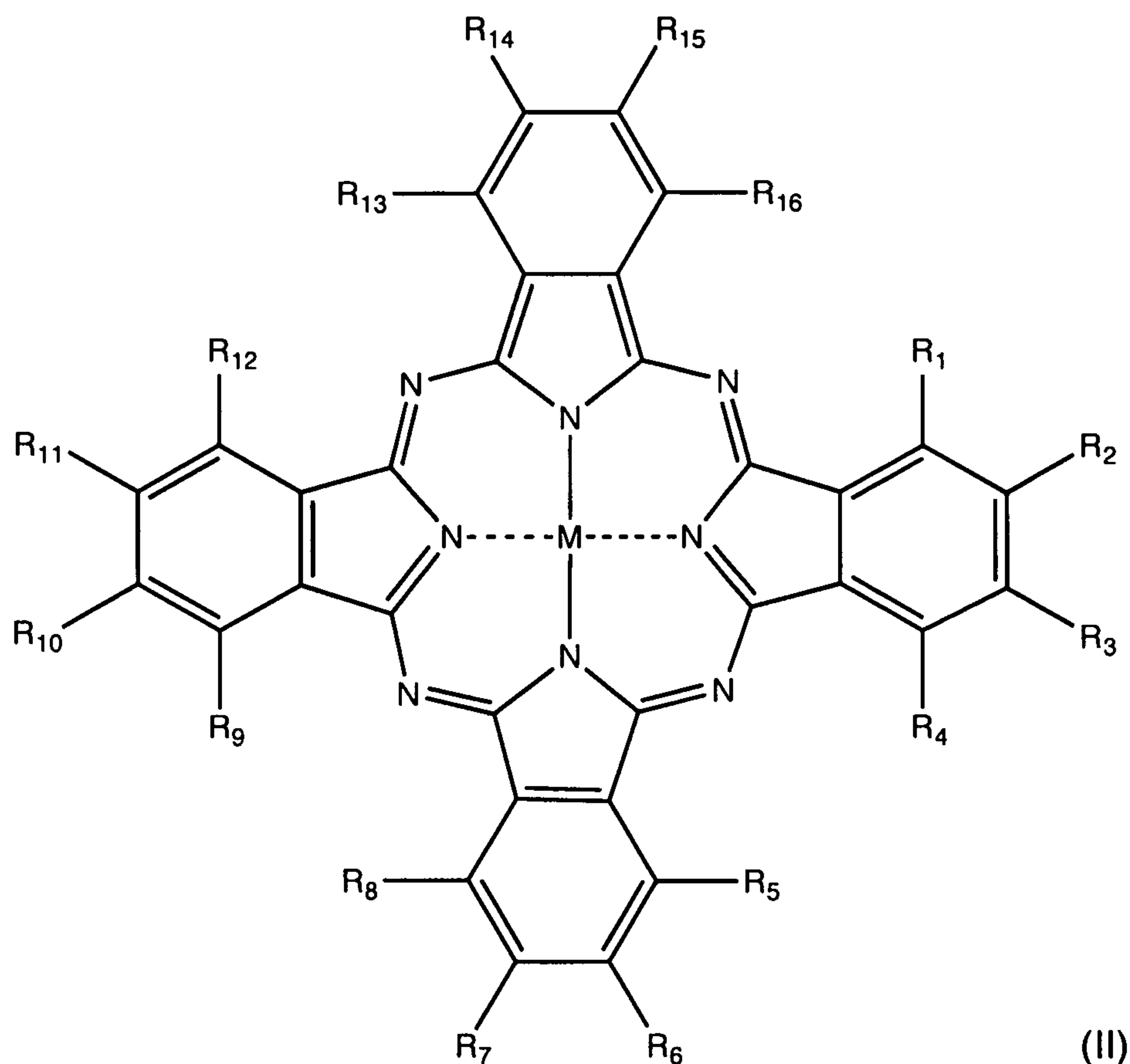


(I)

wherein M comprises a transition metal which is ligated by a tetraazamacrocyclic, such as, for example, substituted porphyrins, unsubstituted porphyrins, substituted phthalocyanines, unsubstituted phthalocyanines, substituted naphthalocyanines, unsubstituted naphthalocyanines, and combinations thereof.

[0048] By way of non-limiting examples, oxygen reduction catalysts may comprise a material resulting from pyrolysis of a compound, a structural isomer of a compound, and/or mixtures of isomers of compounds, represented by the following structure:

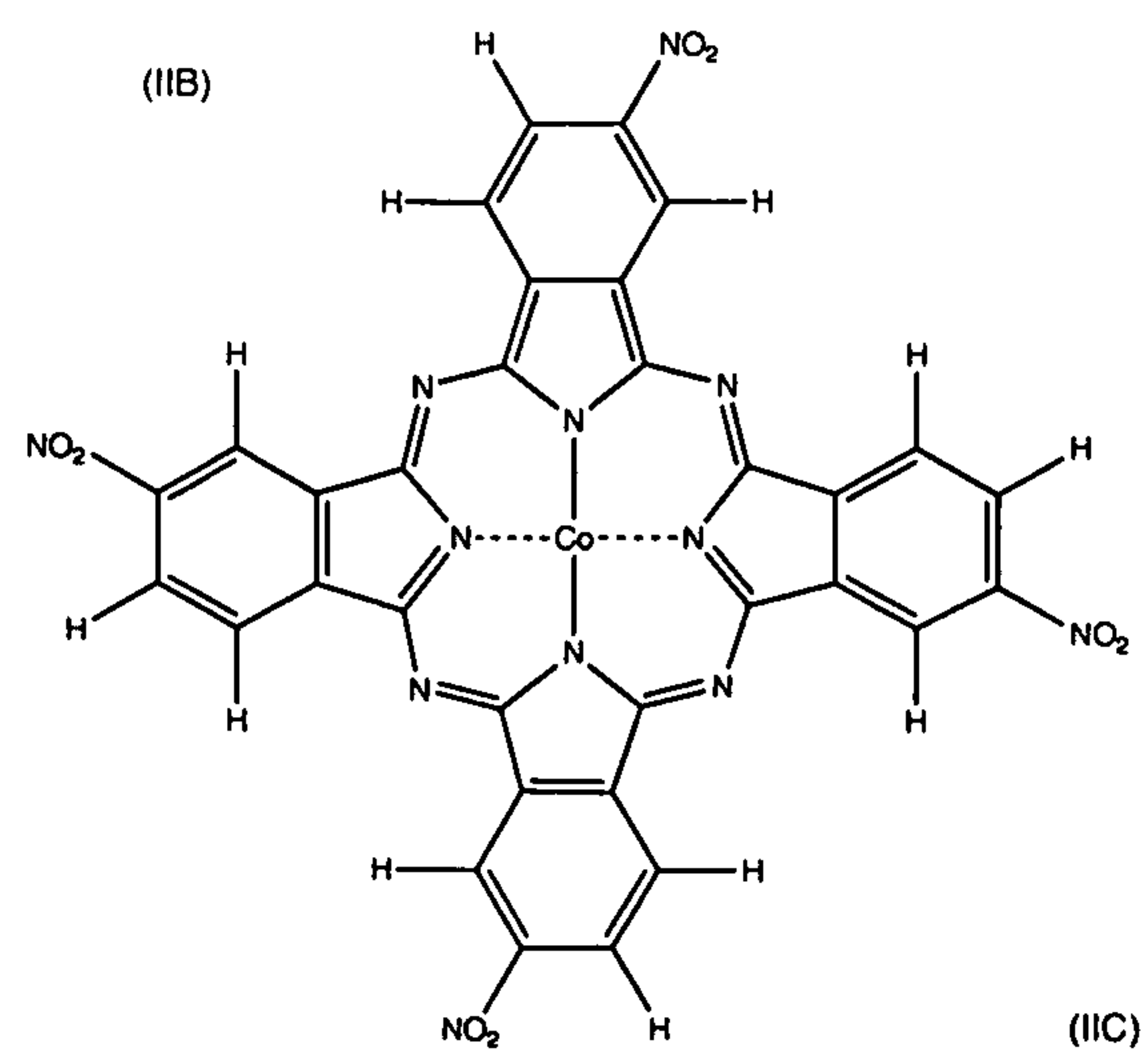
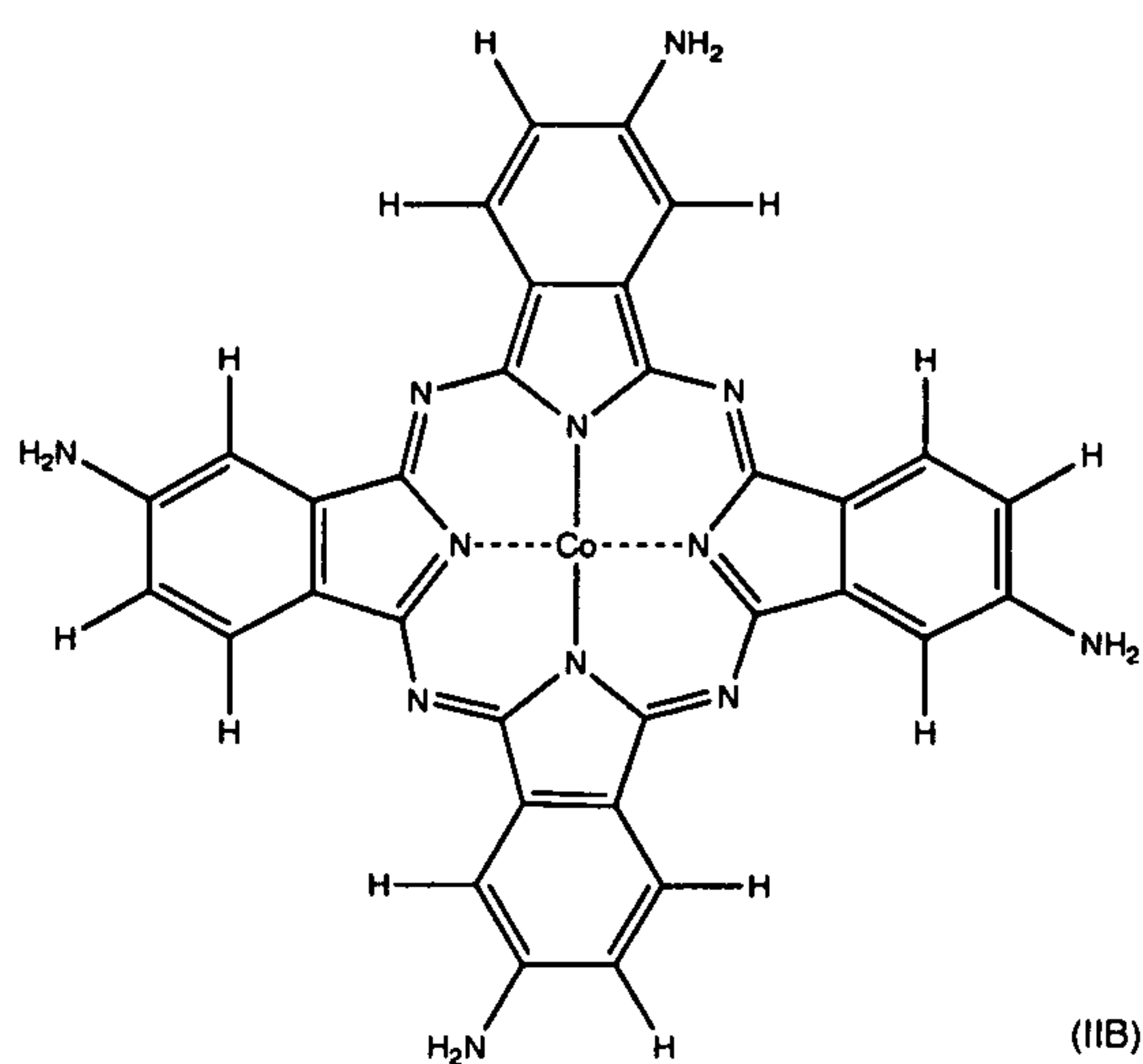
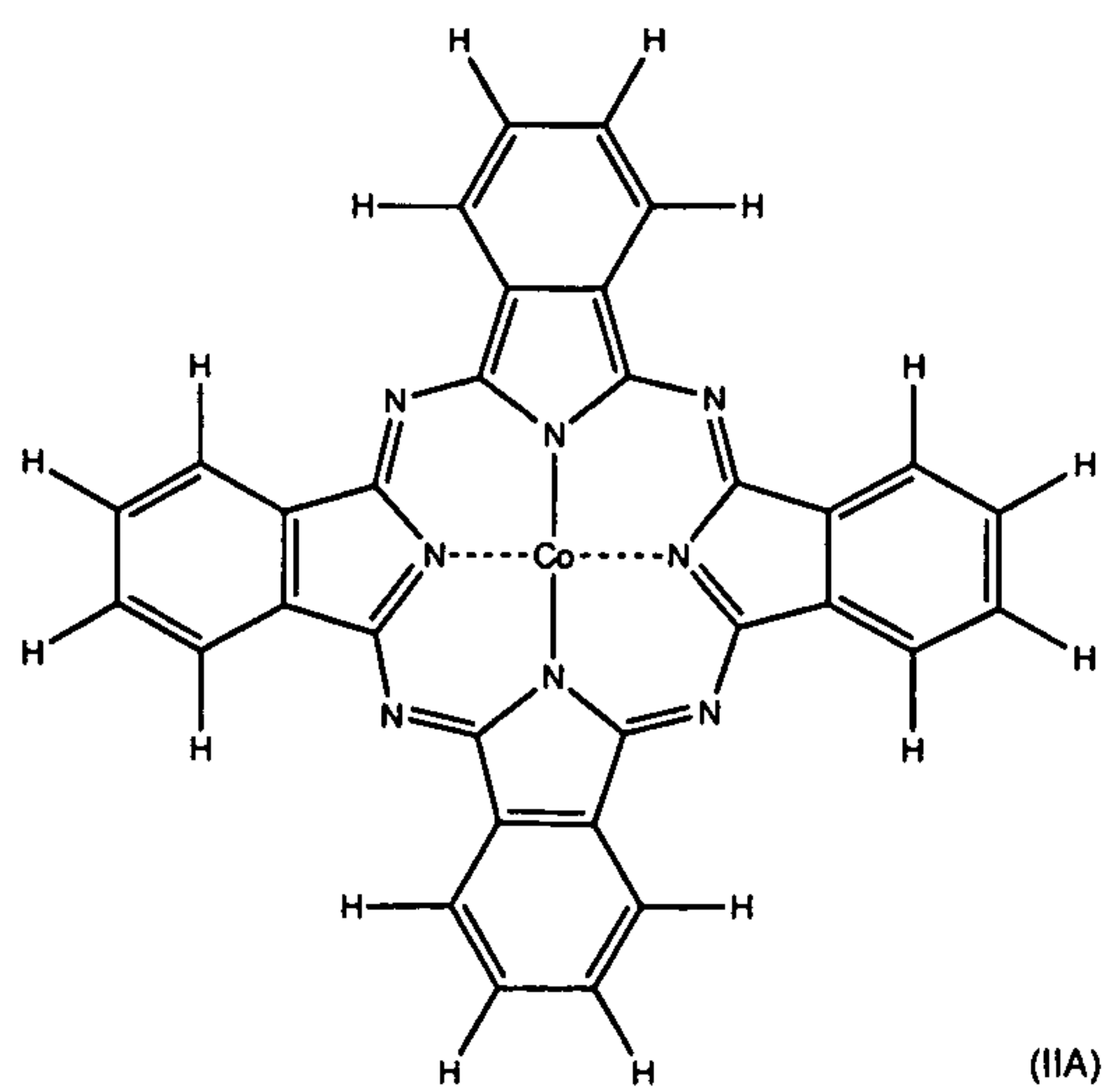
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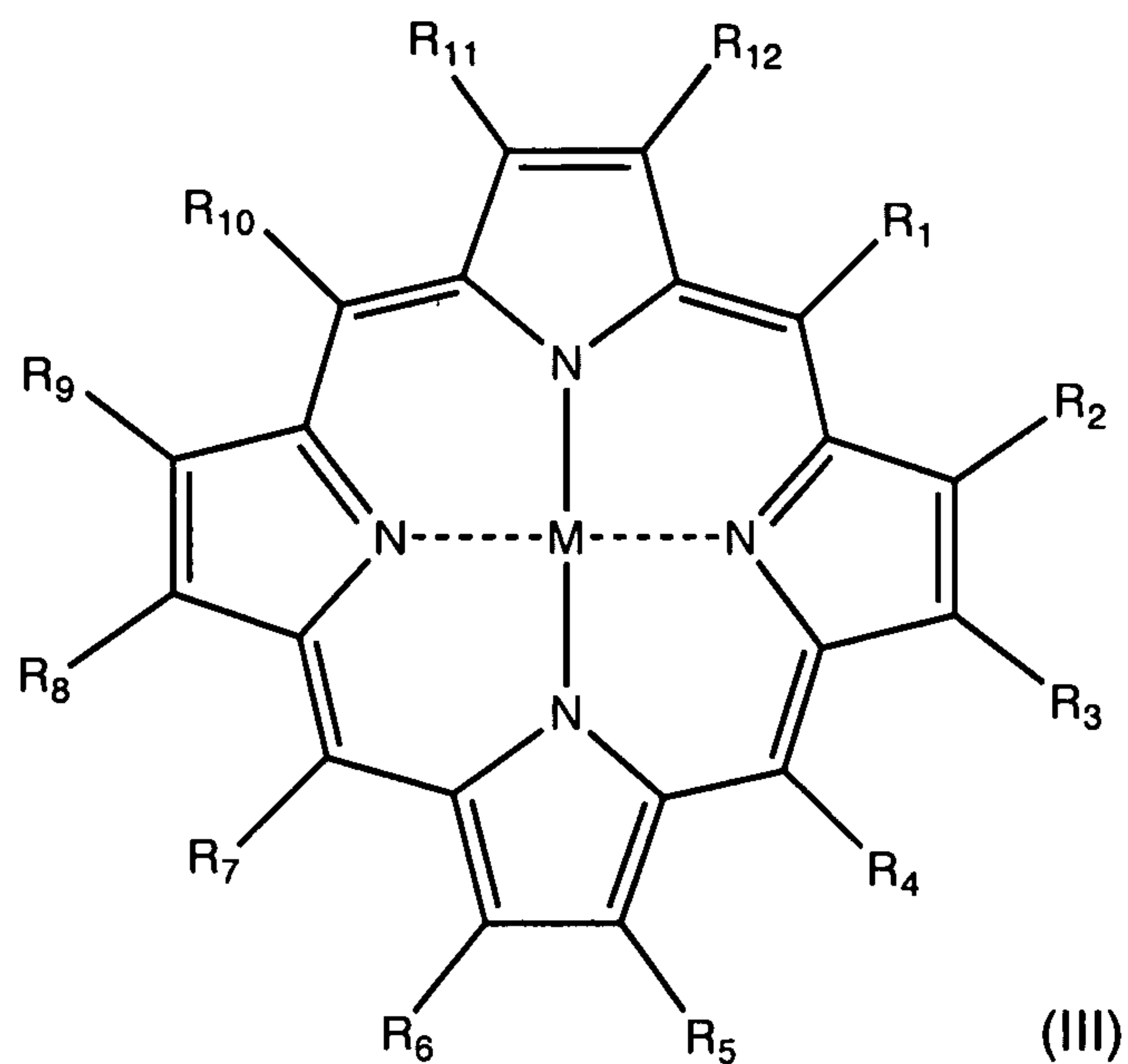
wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{16} are the same or different and comprise H, NO_2 , NH_2 , NHR_{17} , $\text{N(R}_{18})_2$, CO_2H , CO_2R_{19} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{20} , SH, SR_{21} , and combinations thereof; and wherein R_{17-21} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s).

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[0049] Three specific phthalocyanines which serve as oxygen reduction catalysts include:



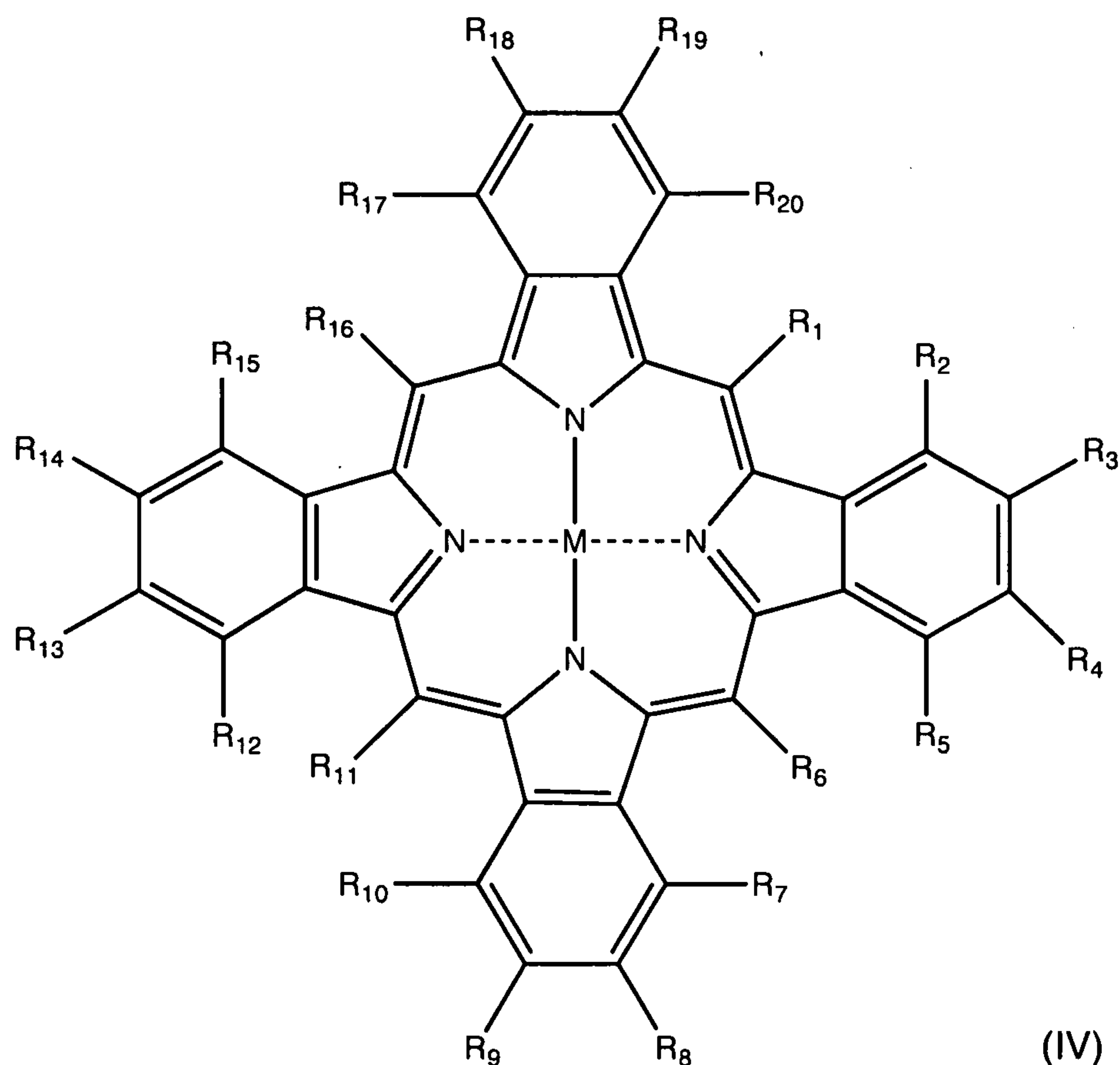
[0050] By way of additional non-limiting examples, oxygen reduction catalysts may comprise a material resulting from pyrolysis of a compound, a structural isomer of a compound, and/or mixtures of isomers of compounds, represented by the following formula:



wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{12} are the same or different and comprise H, NO_2 , NH_2 , NHR_{13} , $\text{N(R}_{14})_2$, CO_2H , CO_2R_{15} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{16} , SH , SR_{17} , and combinations thereof; and wherein R_{13-17} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s).

[0051] In one embodiment of the present invention, the oxygen reduction catalyst comprise a material resulting from pyrolysis of a compound, a structural isomer of a compound, and/or mixtures of isomers of compounds, represented by the following formula:

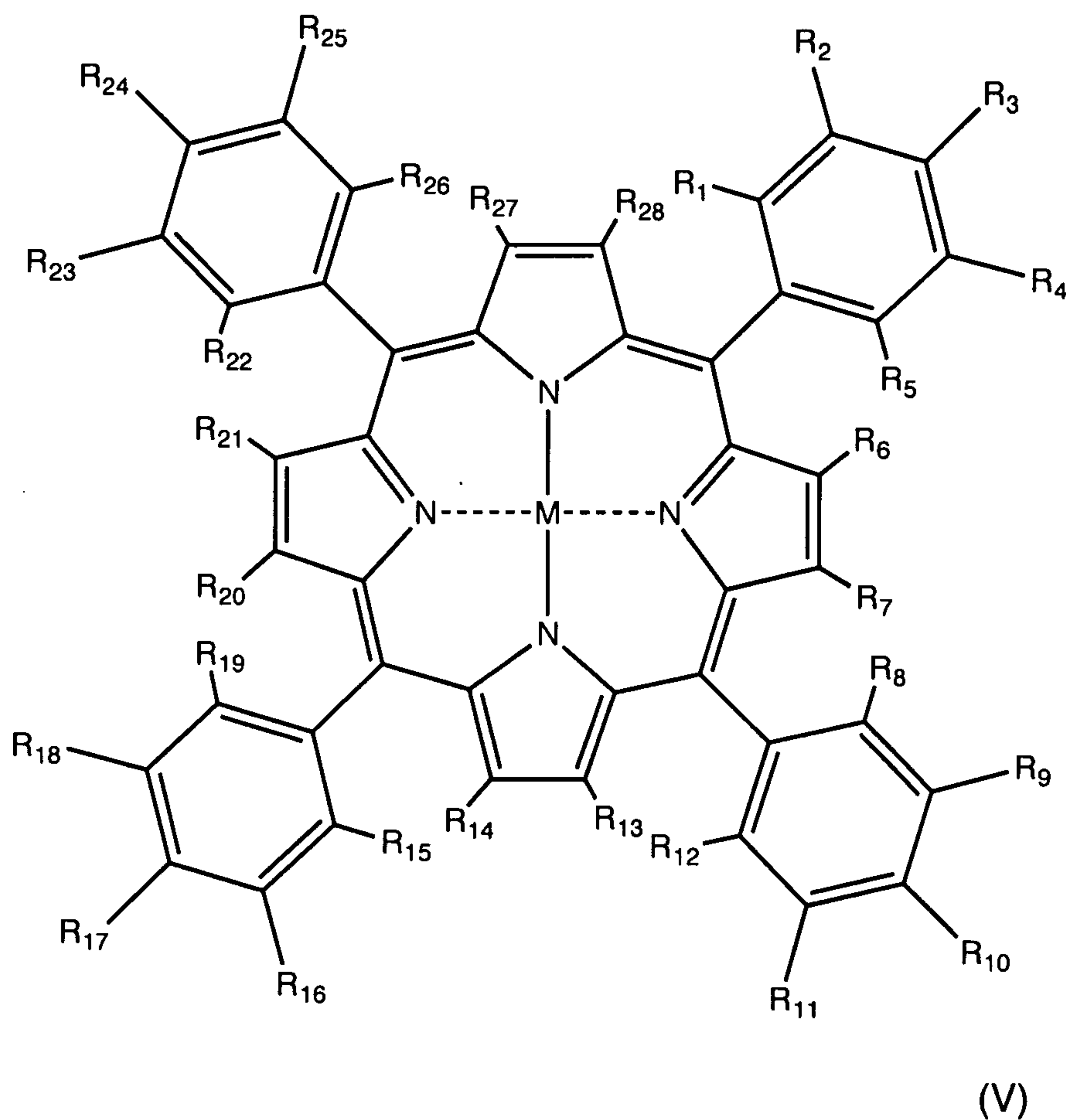
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wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{20} are the same or different and comprise H, NO_2 , NH_2 , NHR_{21} , $\text{N(R}_{22})_2$, CO_2H , CO_2R_{23} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{24} , SH, SR_{25} , and combinations thereof; and wherein R_{21-25} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s).

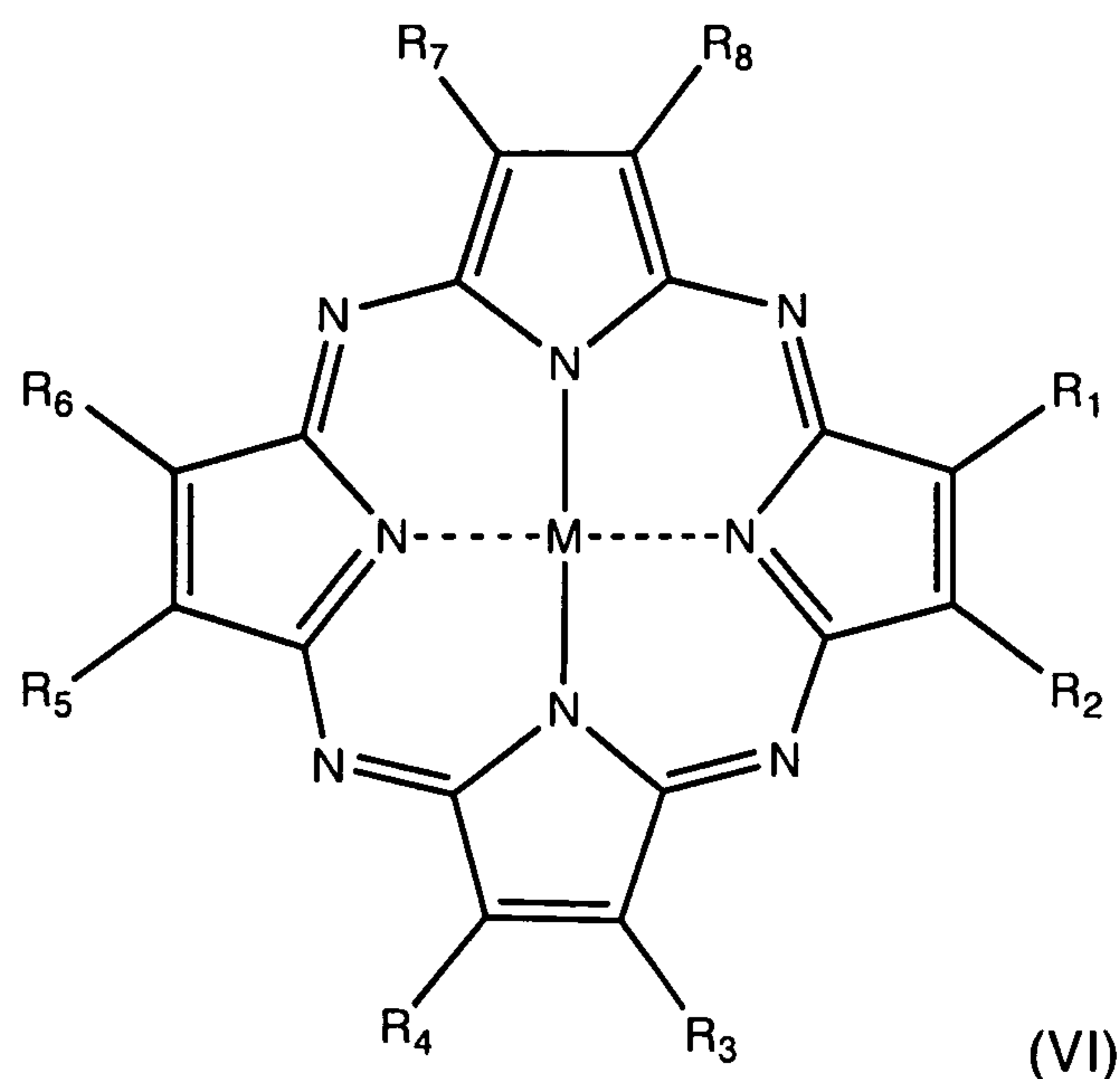
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[0052] In accordance with another embodiment of the present invention, the oxygen reduction catalysts comprises a material resulting from pyrolysis of a compound, a structural isomer of a compound, and/or mixtures of isomers of compounds, represented by the following formula:



wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{28} are the same or different and comprise H, NO_2 , NH_2 , NHR_{29} , $\text{N(R}_{30})_2$, CO_2H , CO_2R_{31} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{32} , SH , SR_{33} , and combinations thereof; and wherein R_{29-33} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s).

[0053] In accordance with yet another embodiment of the present invention, the oxygen reduction catalysts comprise a material resulting from pyrolysis of a compound, a structural isomer of a compound, and/or mixtures of isomers of compounds represented by the following formula:



wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_8 are the same or different and comprise H, NO_2 , NH_2 , NHR_9 , $\text{N(R}_{10})_2$, CO_2H , CO_2R_{11} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{12} , SH, SR_{13} , and combinations thereof; and wherein R_{9-13} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s).

[0054] It will be understood that several of the above-identified compounds are provided herein as working examples and that additional disclosure for the commercial availability and/or preparation of transition metal porphyrins, tetrabenzoporphyrins, tetraphenylporphyrins, tetraazaporphyrins, tetraazamacrocycles, phthalocyanines, naphthalocyanines, bis(phthalocyanines), and bis(naphthalocyanines), are available from common chemical vendors, such as Sigma-Aldrich Chemical Co., of Milwaukee,

Wisconsin and Strem Chemical of Newburyport, Massachusetts.

[0055] Without being bound to any one particular theory, it is believed that the metal atom in M-N₄ catalysts disclosed herein contribute to the proper structural formation of the most active carbon-nitrogen catalytic sites during pyrolysis. As such, removal of the metal after pyrolysis using an acid extraction does not appear to adversely affect electrode performance. Suitable acid extraction techniques are provided in, for example, (T. Ikeda, *et al.*, *J. Phys. Chem. C* 112 (2008) 14706, (M. Saito *et al.*, *215th ECS Meeting*, Abstract #265), and (M. Saito *et al.*, *217th ECS Meeting*, Abstract #502). The Examples *infra* provide further details regarding M-N₄ catalysts.

[0056] Referring once again to Figures 3A-3D, electrochemical sensor preferably includes micro electrode assembly 14, wherein anode 26 and cathode 28 are preferably: (1) disposed upon the same plane, (2) disposed upon the same side of the ion exchange membrane, and/or (3) exposed to a same gaseous environment. It will be understood that, regardless of its ordinary meaning, the term the "same gaseous environment" will be defined herein as the same ambient air, and/or the same air external to the micro electrode assembly. It will be understood that the micro electrode assemblies of the present invention facilitate numerous design configurations not available heretofore. In particular, conventional cathodic materials exhibit catalytic activity for the oxidation of carbon monoxide as well as the reduction of oxygen to water. As such, without restricting the cathode to ambient sample gas, the sensor is susceptible to undesirable failure under a plurality of conditions.

[0057] In accordance with the present invention, micro electrode assembly 14 may be fabricated using any one of a number of conventional techniques, including pad or decal printing, as is disclosed in U.S. Patent No. 5,211,984, brushing, screen printing, spraying, ink jet printing, and/or dip coating - just to name a few.

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[0058] It will be understood that a typical fuel cell or electrochemical sensor has an ion exchange or conducting membrane that separates the two electrodes. Typically this membrane is approximately 10-200 μM thick. However, in certain embodiments of the present invention, ions diffuse laterally across the membrane. A long ion diffusion length increases ionic resistance and therefore reduces signal strength. To reduce any undesirable ionic resistance, the ion diffusion length is preferably minimized between the two electrodes, via a narrow gap, and within each electrode, via narrow electrodes. The cross sectional area between the two electrodes is also preferably maximized to enhance current flow and signal strength. Preferentially, the MEA configuration will comprise an interdigitated electrode design similar to that shown in Figures 3A and 4A.

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[0059] It will be further understood that a typical fuel cell or electrochemical sensor has an electron path length that is essentially the thickness of each electrode which is approximately 1-100 μM , before reaching an external current collector. However, in certain embodiments of the present invention, electrons diffuse laterally across the electrodes before reaching the external current collectors. As such, the carbon based materials have a relatively high electron resistance so the path length is preferably minimized to enhance signal strength. Preferentially, the MEA configuration comprises an interdigitated electrode design similar to that shown in Figures 3A or 4A –

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wherein electrode finger lengths are optimized to reduce the electron resistance but maintain a high amount of material to maximize the rate of chemical reactions occurring.

[0060] In accordance with the present invention, catalysts found in the anode and cathode have different activities and levels of current output towards their respective gases. To reduce wasted material, among other things, the thickness, area, and dimensions of each electrode can be varied. Suitable examples are provided in Figures 3A-3D. Preferably the ratio of the two dimensional areas of the cathode to anode is greater than approximately 1:1, and more preferably approximately 2.4:1. In addition, the ratio of the thickness of the cathode to anode preferably greater than approximately 1:1, and more preferably approximately 2:1. It will be understood that during normal operation (carbon monoxide is present and the sensor is sensing), H₂O is generated at the cathode. At high CO concentrations, the produced water can plug the porous network of the carbon electrode thus reducing the activity of the cathode and reducing the signal strength. A cathode of large surface area can be used to wick this water away from the most active regions of the electrode and allow a stable signal to be achieved.

[0061] As is best shown collectively in Figures 3-5 and Example 15, when a planar design for micro electrode assembly 14 of sensor 10 is utilized, the addition of MWNT to cathodic inks has provided surprisingly beneficial results with respect to enhancing conductivity without adversely affecting catalytic activity.

[0062] Referring now to Figures 4A-4D, electrochemical sensor 10 may also include one or more reference electrodes 40 associated with micro electrode assembly 14. The reference electrodes facilitate, among other things, long term device performance and sensitivity optimization.

[0063] As is best shown in Figure 5, micro electrode assembly 14 preferably includes key member(s) 42, which regulate orientation and positional engagement relative to housing 12 of electrochemical sensor 10. For example, key member 42 may comprise one or more tabs and/or slots, which matingly correspond to housing 12 for proper positioning during, for example, replacement of micro electrode assembly 14.

[0064] In accordance with the present invention sensors preferably comply with alarm specifications set forth in UL 2034.

[0065] It will be understood that, unless otherwise specified, the chemical reagents and compounds provided herein below, or their precursors, are available from common commercial chemical vendors, such as Sigma-Aldrich Chemical Co., of Milwaukee, Wisconsin.

[0066] The invention is further described by the following examples.

EXAMPLE 1

Preparation of Tetranitro(Cobalt Phthalocyanine), CoPc(NO₂)₄

[0067] A 250 mL 3-neck round bottom flask fitted with a thermocouple and reflux condenser was charged with cobalt sulfate heptahydrate (3.4g, 12.1 mmol), 4-nitrophthalic acid (9.25g, 43.8 mmol), urea (15g, 250 mmol), ammonium chloride (1.13g, 21.1 mmol), and ammonium molybdate tetrahydrate (0.14g, 0.1 mmol) in 6.5 mL nitrobenzene. The mixture was heated to 185°C for 5 hours under a blanket of nitrogen. The reddish mixture quickly turned dark blue. The solid was collected on a glass frit filter and washed with 350 mL of warm methanol to remove residual nitrobenzene. The solid was then boiled in 150 mL 1M HCl saturated with NaCl for five minutes. The liquid was removed by filtration then the solid was added to 150 mL 1M NaOH plus 50g NaCl. The mixture was heated to 90°C under a light argon flow until ammonia was no longer

evolved as checked with damp pH paper. The mixture was cooled and the solid collected by filtration. The solid was alternately washed three times with 1.0M HCl (60 mL) then 1.0M NaOH (60 mL). This was followed by washing with 400 mL water. The solid was dried in a vacuum oven at 70°C for 24 hours. Yield: 7.86g = 86%

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EXAMPLE 2

Preparation of Tetraamino Cobalt Phthalocyanine, CoPc(NH₂)₄

[0068] A 50 mL round bottom flask fitted with a condenser was charged with CoPc(NO₂)₄ (0.68g, 0.9 mmol) and sodium sulfide monohydrate (10.4g, 43.4 mmol) in 15 mL water. The mixture was stirred at room temperature for 72 hours then heated to reflux for 24 hours. After cooling to room temperature, a blue solid was collected by filtration. The solid was washed with 50 mL water then it was dissolved in 100 mL 1M HCl. A small amount of insoluble material was removed by filtration. The filtrate was collected and the pH was raised to > 11 by the very careful addition of NaOH pellets. A large amount of greenish-blue precipitate formed which was collected by filtration and washed with copious amounts of water until the filtrate was neutral by pH paper. The solid was dried in a vacuum oven at 70°C for 24 hours. Yield: 0.28g = 49%

EXAMPLE 3

Cobalt Phthalocyanine Deposited and Thermally

Treated on Multi-walled Carbon Nanotubes, CoPc-MWNT

20 [0069] A 50 mL round bottom flask was charged with 100 mg cobalt phthalocyanine (Aldrich), 200 mg MWNT(Cheap Tubes Inc., 10-20 nm diameter, 10-30 μM length, > 95% purity), and 25 mL dry DMF. The mixture was sonicated for 40 minutes (750W, 38% amplitude, 20 seconds on/10 seconds off pulse). The DMF was removed by rotary evaporation. The purple tinted tubes were dried in a vacuum oven at

70°C for 24 hours. The CoPc deposited tubes (299mg) were placed in a fused quartz boat and inserted into a tube furnace. The furnace was purged with argon (275 mL/min) for 45 minutes. The argon flow was reduced to 100 mL/min then the furnace was heated to 700°C. That temperature was held for two hours then cooled to room temperature.

5 Final yield: 273mg. Thermogravimetric analysis, TGA yielded 6.03 wt% residue.

EXAMPLE 4

Metal-free Phthalocyanine Deposited and Thermally

Treated on Multi-wall Carbon Nanotubes, Pc-MWNT

[0070] A 250 mL conical flask was charged with 222 mg 29H,31H-phthalocyanine (Aldrich), 667 mg MWNT (Cheap Tubes Inc., 10-20 nm diameter, 10-20 μ M length, > 95% purity), and 150 mL anhydrous DMF. The mixture was sonicated for 30 minutes (750W, 50% amplitude, 30 seconds on/10 seconds off pulse) while in an ice bath. The suspension was poured into 800 mL 1:1 hexane/ethyl ether with vigorous stirring. The solid was collected on a 0.45 μ M PTFE membrane filter and washed with

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15 two portions of 250 mL 1:1 hexane/ethyl ether. The material was transferred to a fused quartz boat and placed in a tube furnace. The solid was dried at 100 °C under a flow of anhydrous argon at 235 mL/min for 90 minutes. The argon flow was reduced to 65 mL/min then the temperature ramped to 700 °C and held there for 120 minutes. After cooling to room temperature, 730 mg of catalyst was yielded.

EXAMPLE 5

Sample Preparation, CoPc(NH₂)₄-MWNT/Nafion

[0071] 5.0mg CoPc(NH₂)₄-MWNT was suspended in 10.0 mL 1:1 ethanol/water. The mixture was sonicated for 10 minutes (750W, 30% amplitude, 20sec on/10sec off pulse). 40.0 μ L 5% Nafion solution was added. The suspension was sonicated for an

additional 2 minutes under the above conditions. 20.0 μL of the black suspension was carefully deposited onto only the glassy carbon of a RDE electrode (Pine Instruments, 5.0 mm diameter) and allowed to dry. All samples were prepared in a similar manner.

Experimental Parameters

5 [0072] 0.5M H_2SO_4 was used as an electrolyte. The counter electrode was platinum mesh and the reference electrode was a double junction Ag/AgCl electrode.

Initial Activities for Oxygen Reduction by Cyclic Voltammetry

[0073] The electrolyte was purged with oxygen then the sample was scanned from 1.0 to -0.2V at 10 mV/s to determine the initial activity of the sample. This was
10 repeated for several cobalt phthalocyanines on both MWNT and commercially available XC72 carbon. A state of the art fuel cell catalyst, 10 wt% Pt/XC72 (E Tek) was also included as was 5 wt% Pt/carbon (Aldrich). See Figure 6 for results. Activity is determined by the onset of current. As shown in Figure 6, the 10 wt% Pt/XC72 was the most active though all the cobalt based catalysts were nearly as active, which verifies
15 that a broad spectrum of novel cobalt based catalysts exhibit sufficient electrochemical activity. The nitrogen doped nanotubes, N-MWNT, showed very little activity.

Carbon Monoxide Activity

[0074] Unlike platinum based catalysts which are active in both the reduction of oxygen and the oxidation of various fuels, such as hydrogen, methanol, or carbon
20 monoxide, the cobalt-nitrogen based catalysts disclosed herein have been developed to operate only as ORR catalysts. To check for activity for the catalytic oxidation of carbon monoxide, a sample of $\text{CoPc}(\text{NO}_2)_4\text{-XC72/Nafion}$ was studied. Identical conditions to study the ORR activity were used with the exception that the electrolyte was purged with carbon monoxide for 30 minutes. The sample was scanned from -0.2 to 1.0 to -0.2V at

EXAMPLE 6

EXAMPLE 7

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PTFE membrane filter. The product was washed with 100 mL ethanol then dried in a vacuum oven at 70 °C for 16 hours. TGA yielded 10.5 wt% Pt.

EXAMPLE 8

Preparation of Anodic Catalyst II

5 [0077] 9.6 wt% Pt/PCA-MWNT: A 1-L Erlenmeyer flask was charged with 1.25g
PCA-MWNT in 540 mL 5% H₂O in ethylene glycol. The modified nanotubes were
suspended in the solvent by sonication for 120 minutes (750W, 50% amplitude, 30 s
on/10s off pulse). The suspension was transferred to a 1-L round bottom flask. A
magnetic stir bar was added to the flask. Under vigorous stirring, 347 mg H₂PtCl₆
10 (Sigma-Aldrich, 40 wt% Pt) in 10 mL 5% H₂O in ethylene glycol was added over one
minute. Stirring was continued for 2 hours. The flask was then fitted with a reflux
condenser under a blanket of nitrogen and placed in microwave (Milestone Ethos,
1200W). Under full power and magnetic stirring, the suspension temperature was
ramped to reflux at 165°C in 4 minutes and was held there for an additional 8 minutes.
15 After cooling to room temperature, the suspension was diluted with 500 mL ethanol then
collected by filtration on a 0.45μM PTFE membrane filter. The filtrate was washed with
two portions of 200 mL ethanol each followed by drying under vacuum at 70°C for 16
hours. TGA yielded 9.6 wt% Pt. Powder XRD on a similarly prepared sample yielded an
average Pt nanoparticle size of 3.3nm by examination of the Pt[200] peak.

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EXAMPLE 9

Preparation of Anode Ink

[0078] 10.2 wt% Pt/PCA-MWNT was finely ground using an agate mortar and
pestle. A 125 mL Erlenmeyer flask was charged with 254 mg 10.2 wt% Pt/PCA-MWNT,
6.5g glycerol (Sigma-Aldrich), 865 mg water (18.2 MΩ-cm, Millipore), and 8.5 g 1-

propanol (Sigma-Aldrich). Approximately 60 g of excess 1-propanol was then added. The catalyst was suspended by sonication for 60 minutes (750W, 50% amplitude, 30s on/10s off pulse). 850 mg Nafion solution (10wt% in H₂O, Fuel Cell Store) diluted in 11 g 1-propanol was added to the suspension. The suspension was sonicated for an additional five minutes under the conditions listed previously. A magnetic stir bar was placed in the flask and the suspension was vigorously stirred for 16 hours. The suspension was transferred to a tared bottle and concentrated using heat and a flow of dry argon, until 2 wt% solids was reached. 80 μ L tetrabutylammonium hydroxide (TBA-OH) (1.0M in methanol, Sigma-Aldrich) was added to covert the acidic Nafion to the heat stable TBA⁺ form. After removal of volatiles, an electrode consisting of 67 wt% (Pt/PCA-MWNT) and 33 wt% Nafion results.

EXAMPLE 10

Preparation of Cathode Ink

[0079] A 250 mL pear shaped flask was charged with 150 mg CoPc(NO₂)₄-MWNT, 150 mg MWNT (Cheap Tubes Inc., Brattleboro, VT), 83 mg PTFE dispersion (0.1-1.0 μ M, 60 wt% in H₂O, Ion-Power Inc.), 9.60g glycerol, 2.09g H₂O, and 12.18g 1-propanol. Approximately 125 g of excess 1-propanol was added. The mixture was sonicated for 120 minutes (750W, 50% amplitude, 30 s on/10s off pulse) while cooled in an ice bath. A magnetic stirbar was added to the suspension and under vigorous stirring, 668 mg Nafion solution (15 wt% in aqueous alcohols, Liquion LQ-1115, Ion-power Inc., New Castle, DE) was added. The suspension was mixed for two hours then sonicated for five minutes under the above conditions. 141 μ L tetrabutylammonium hydroxide solution (1.0M in methanol, Sigma-Aldrich) was added then the suspension was sonicated for five minutes under the above conditions. The suspension was

concentrated by rotary evaporation then transferred to a tared bottle and concentrated further with heat until a 2 wt.% solids suspension was achieved. After removal of volatiles, an electrode consisting of 30.0 wt% (33% Co(Pc(NO₂)₄/MWNT), 30.0 wt% MWNT, 20 wt% Nafion, and 20 wt% PTFE results.

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EXAMPLE 11

Preparation of Na⁺-Nafion 117

[0080] A 8 cm x 11 cm piece of Nafion 117 membrane (Dupont) was placed in 275 mL water purified by reverse osmosis at 90°C for 120 minutes. The membrane was quickly rinsed with water then placed in 275 mL 3% H₂O₂ at 90°C for 60 minutes. The
10 membrane was rinsed with water for 10 minutes then converted to the Na⁺ form by placing it into 275 mL 1M NaOH for 120 minutes. The membrane was rinsed with water for 15 minutes and allowed to air dry. After cutting into pieces of the desired size, it was stored at room temperature in water (18.2 MΩ-cm, Millipore).

EXAMPLE 12

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Decal Preparation

[0081] A stamp of pattern similar to Figure 3C is machined from a 1 cm thick block of Teflon. The stamp dimensions are approximately 1 cm x 0.7 cm with a 0.1 cm gap between the two electrodes. A light coating of PTFE mold release is applied to the stamp. Using a micropipette, anodic ink (10% Pt/PCA-MWNT/Nafion, 2 wt% solids) is
20 applied to the anode in a volume of 100-1000 μL/cm², preferably 150-300 μL/cm². Using a micropipette, cathodic ink (1:1(33% Co(Pc(NO₂)₄/MWNT)/MWNT/Nafion, 2 wt% solids) is applied to the cathode in a volume of 100-1000 μL/cm², preferably 150-300 μL/cm². The stamp is dried at 50-250°C, preferably 180°C. A flow of dry nitrogen across the part or application of vacuum may be used in addition to heat to speed drying of the ink. A

second layer of anodic ink is applied to the anode for a total of two. Three additional layers of cathodic ink is applied to the cathode for a total of four. Identical drying procedures as listed previously are used to dry each individual layer of ink.

EXAMPLE 13

5 Heat Pressing Decal onto Ion-Exchange Membrane

[0082] A 1.5 cm x 1.5 cm piece of Nafion 117 membrane (Dupont) in the Na⁺ form is placed on top of the decal coated Teflon stamp. A piece of PTFE coated stainless steel sheet is placed on top the ion-exchange membrane. The assembly is then placed in a heat press set to 195°C. Pressure (47atm) is applied to the assembly for
10 120 seconds. The assembly is removed from the press and allowed to cool. The ion-exchange membrane is slowly peeled away from the Teflon stamp. Ideally all of the ink will have transferred from the stamp to the membrane.

EXAMPLE 14

MEA Acidification and Rehydration

15 [0083] The prepared MEA is placed into a volume of 20-100 mL of 0.1M H₂SO₄. It is heated to 60-100°C, preferably 80-90°C for 1-16 hours. The 0.1M H₂SO₄ is decanted and this step may optionally be repeated. The MEA is then rinsed with H₂O purified by reverse osmosis and placed into a volume of 20-100 mL of H₂O. It is heated to 60-
20 100°C, preferably 80-90°C for 1-16 hours. The MEA is rinsed a final time with H₂O purified by reverse osmosis then stored flat between two absorbent sheets until use.

EXAMPLE 15

Addition of MWNT to Cathodic Inks

[0084] A stamped electrode on a Nafion membrane prepared from a 2 wt% solids ink containing 1.5 wt% (20% Co(Pc(NO₂)₄/MWNT) and 0.5 wt% Nafion resulted in

an average resistance of 35-70 kΩ/cm. To reduce the resistance of the electrodes, some of the catalytic carbon material was replaced with pure MWNT. A stamped electrode of similar cross-sectional area on a Nafion membrane was prepared from a 2 wt% solids ink containing 0.75 wt% (33% Co(Pc(NO₂)₄/MWNT), 0.75 wt% MWNT (Cheap Tubes Inc., 10-20 nm diameter, 10-30 μM length, >95% purity) and 0.5 wt% Nafion. The average resistance was 2 kΩ/cm. Both electrodes contained approximately the same amount of cobalt-N₄ catalyst. It was discovered that that the pyrolysis step dramatically decreased the conductivity of the MWNT carbon support – possibly due to coating the tubes with CoPc(NO₂)₄ which is then pyrolyzed to form a catalytically active but electrically insulating layer of partially-graphitized carbon and nitrogen along with a small amount of cobalt. This coating which has a lower electronic conductivity than the original, highly graphitic MWNT. By blending the pyrolyzed catalyst with pure MWNT, the electronic conductivity can be enhanced without affecting the catalytic activity.

EXAMPLE 16

Addition of PTFE to Cathodic Inks

[0085] In the cathode of a fuel cell or sensor, H₂O is typically generated. At high currents normally found in fuel cells, this H₂O can cause flooding of the pores within the electrode and effectively reduce the amount of oxygen that can reach the catalyst active sites. Known solutions include careful regulation of the flow rate and/or humidity in the oxygen or air feed which requires a sophisticated level of control and supplementary equipment. Though sensors never operate under high current conditions like fuel cells, they have near zero rates of airflow which limits the removal of excess water by evaporation. Sensors are also open systems, exposed to the environment, and must deal with variations in ambient humidity. As such, a sophisticated level of control and

supplementary equipment is not an option in a typical sensor application. A simplified method of addressing the removal of excess H₂O in gas sensors is to make the electrode more hydrophobic by the addition of PTFE. Suitable PTFE addition techniques are provided in, for example, U.S. Patent No. 6,800,391. Moreover, with the addition of PTFE, pore sizes within the electrode and the availability of the gas to the active site can be controllably modified.

EXAMPLE 17

Performance of Sensors I and II

10 [0086] As is shown in Figures 8A and 8B, both Sensors I and II, which were fabricated in accordance with the present invention, exhibited well defined performance characteristics toward compliance with alarm specifications set forth in UL 2034.

EXAMPLE 18

Sensor Calibration

15 [0087] As is shown in Figure 9, sensors prepared in accordance with the present invention can surprisingly be calibrated with an ideal two-point calibration. It will be understood that normal sensor calibrations require mathematical fits having computations substantially more complex than the displayed linear calibration.

[0088] While the invention has been described in detail herein in accordance with certain preferred embodiments thereof, many modifications and changes therein may be effected by those skilled in the art. Accordingly, it is our intent to be limited only by the scope of the appending claims and not by way of details and instrumentalities describing the embodiments shown herein.

20

CLAIMS:

1. An electrochemical carbon monoxide sensor for use in a gas/fire detector, said electrochemical carbon monoxide sensor being exposed to a sample gas during normal sensing operation, the sensor comprising:

a housing, wherein the housing comprises a first sidewall, a second sidewall, a top wall, and a bottom wall, and wherein the first sidewall, the second sidewall, the top wall and the bottom wall define a containment region for containing a micro electrode assembly therein, and further wherein the top wall of the housing comprises a gaseous diffusion aperture, and further wherein the housing is void of a solvent reservoir;

wherein:

the micro electrode assembly comprises an anode, a cathode and an ion conducting membrane, and wherein the ion conducting membrane permits ion transport between the anode and the cathode, and wherein the ion conducting membrane prevents electron conduction between the anode and the cathode, and further wherein the ion conducting membrane comprises at least one of an acid doped polybenzimidazole, an acid doped polypyridylbenzimidazole, a protic ionic liquid doped polybenzimidazole, a protic ionic liquid doped sulfonated polyimide, a polyfluorinated sulfonic acid, or combinations thereof;

the cathode comprises an oxygen reduction catalyst that comprises a pyrolysis product of a carbonaceous material and an organometallic coordination complex of a transition metal with a nitrogen containing macrocycle that has been deposited on the carbonaceous material; and

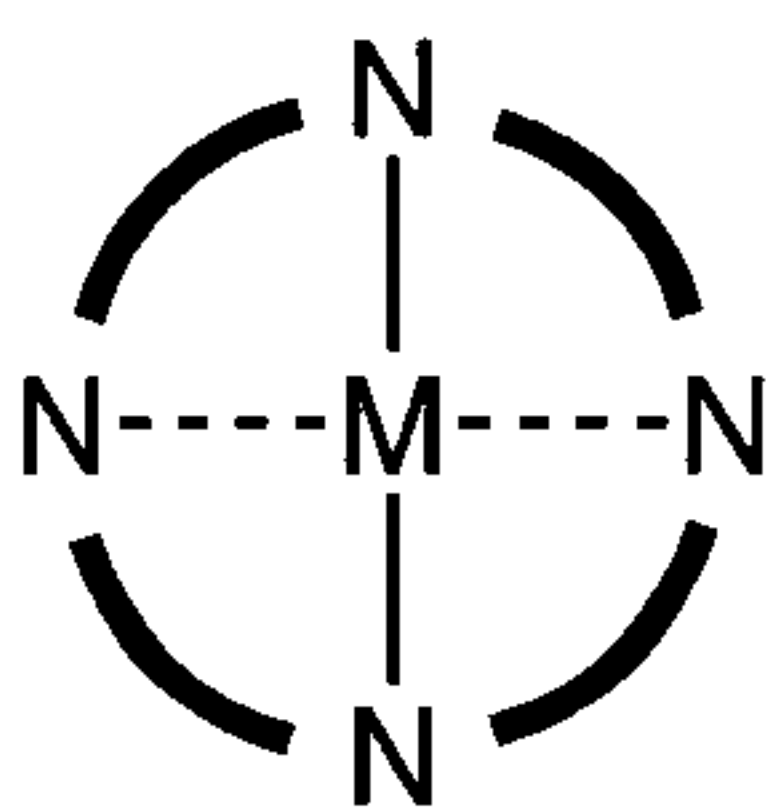
wherein the anode and the cathode are configured to be exposed to the same sample gas during normal sensing operation.

2. The electrochemical carbon monoxide sensor according to claim 1, wherein the organometallic coordination complex comprises at least one of the group comprising substituted transition metal porphyrins, unsubstituted transition metal porphyrins, substituted transition metal tetrabenzoporphyrins, unsubstituted transition metal tetrabenzoporphyrins, substituted transition metal tetraphenylporphyrins, unsubstituted transition metal tetraphenylporphyrins, substituted transition metal tetraazaporphyrins, unsubstituted transition metal tetraazaporphyrins, substituted transition metal

tetraazamacrocycles, unsubstituted transition metal tetraazamacrocycles, substituted transition metal phthalocyanines, unsubstituted transition metal phthalocyanines, substituted transition metal naphthalocyanines, unsubstituted transition metal naphthalocyanines, substituted transition metal bis(phthalocyanines), unsubstituted transition metal bis(phthalocyanines), substituted transition metal bis(naphthalocyanines), unsubstituted transition metal bis(naphthalocyanines), and combinations thereof.

3. The electrochemical carbon monoxide sensor according to claim 1, wherein the organometallic coordination complex comprises at least one of the group comprising substituted cobalt porphyrins, unsubstituted cobalt porphyrins, substituted cobalt tetrabenzoporphyrins, unsubstituted cobalt tetrabenzoporphyrins, substituted cobalt tetraphenylporphyrins, unsubstituted cobalt tetraphenylporphyrins, substituted cobalt tetraazaporphyrins, unsubstituted cobalt tetraazaporphyrins, substituted cobalt tetraazamacrocycles, unsubstituted cobalt tetraazamacrocycles, substituted cobalt metal phthalocyanines, unsubstituted cobalt phthalocyanines, substituted cobalt naphthalocyanines, unsubstituted cobalt naphthalocyanines, substituted cobalt bis(phthalocyanines), unsubstituted cobalt bis(phthalocyanines), substituted cobalt bis(naphthalocyanines), unsubstituted cobalt bis(naphthalocyanines), and combinations thereof.

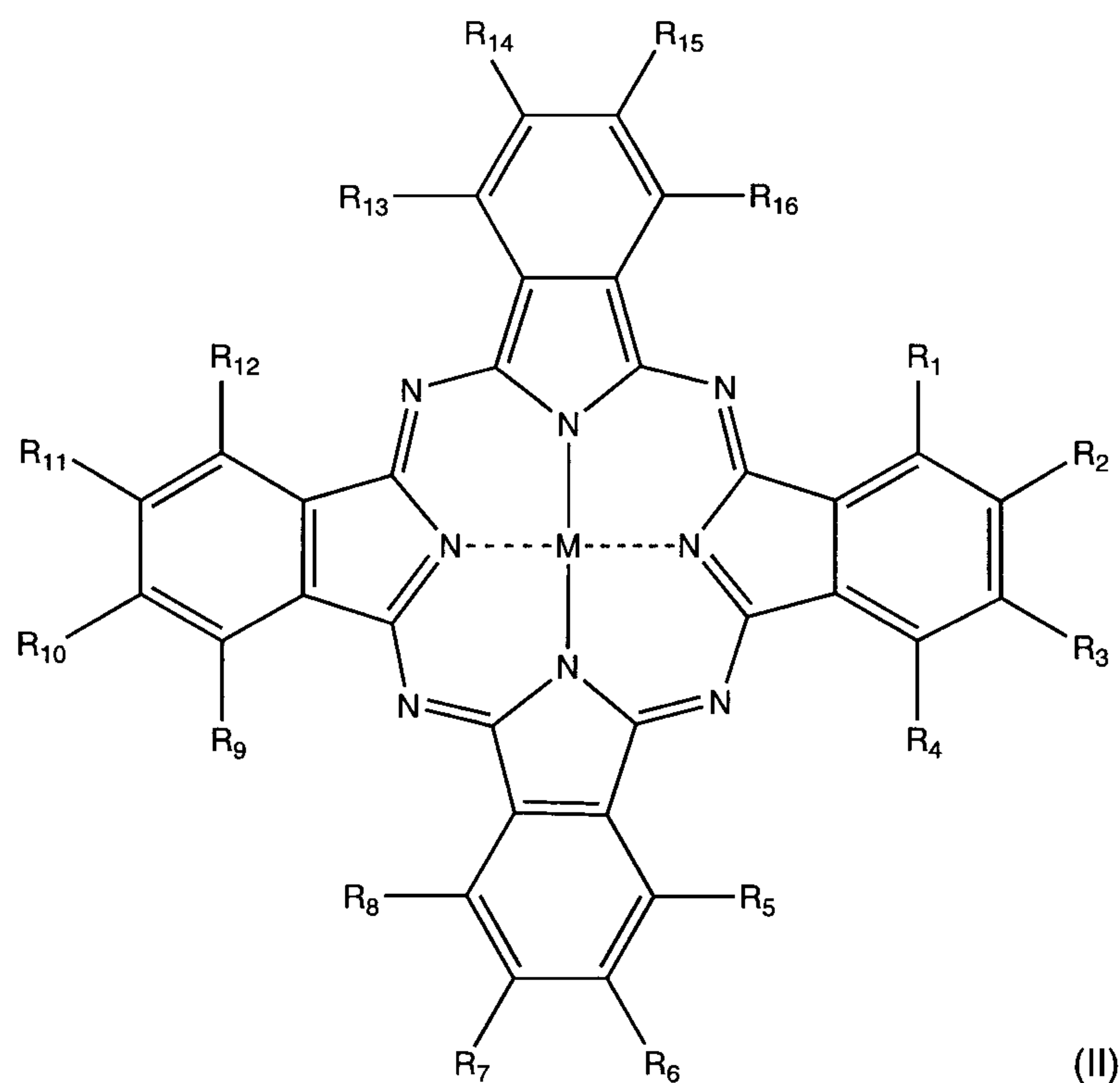
4. The electrochemical carbon monoxide sensor according to claim 1, wherein the organometallic coordination complex comprises a compound of formula (I):



(I)

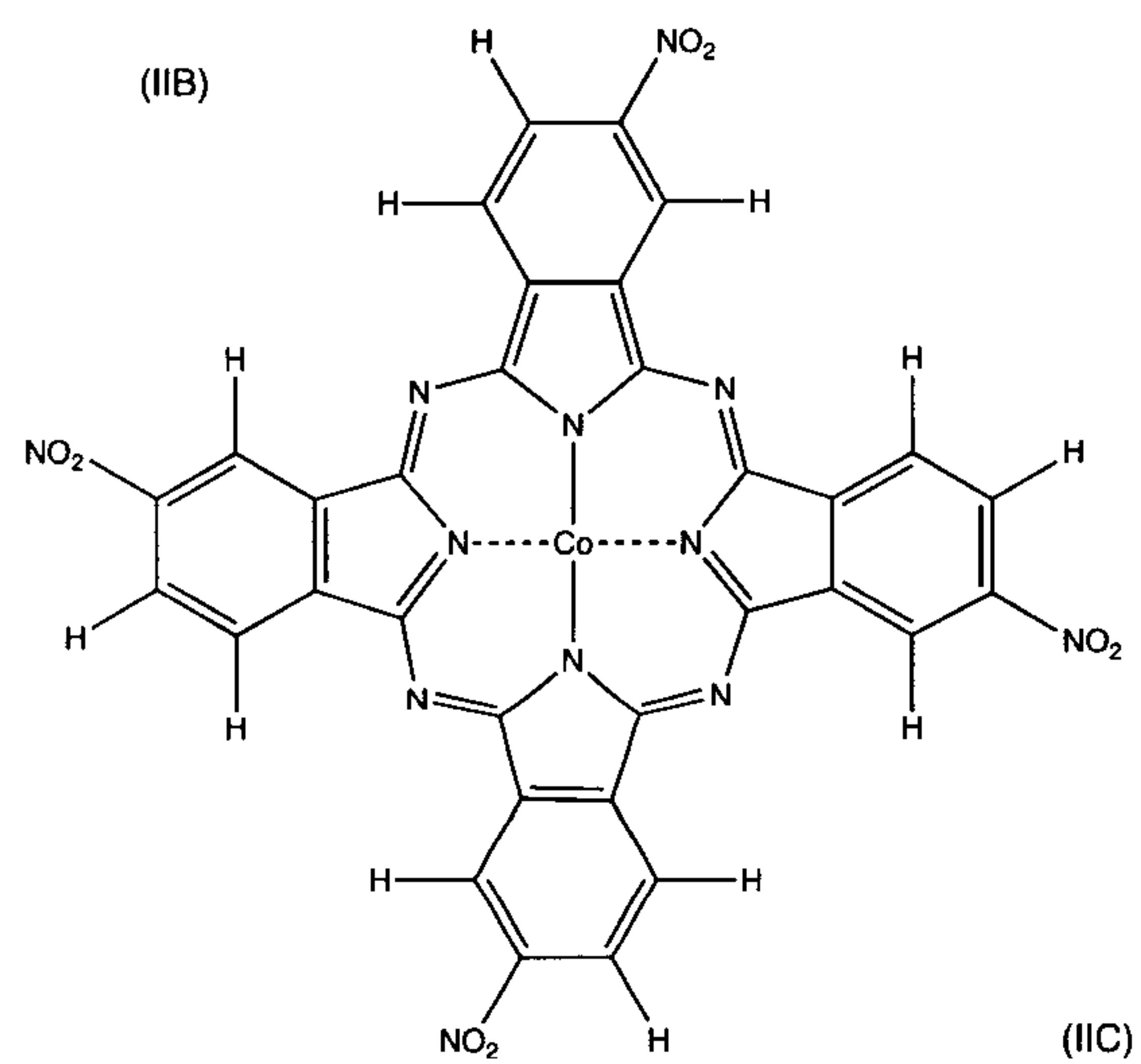
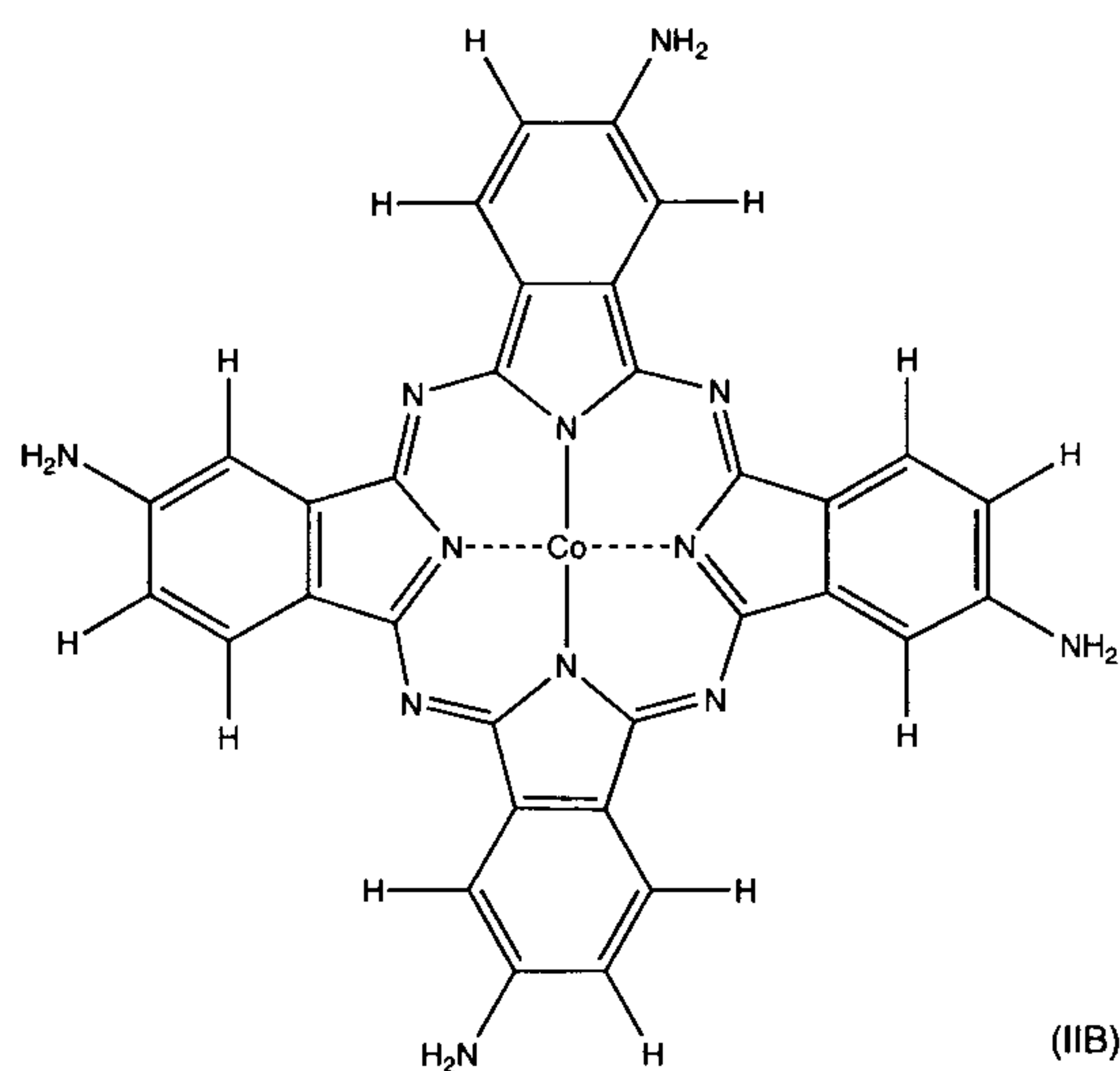
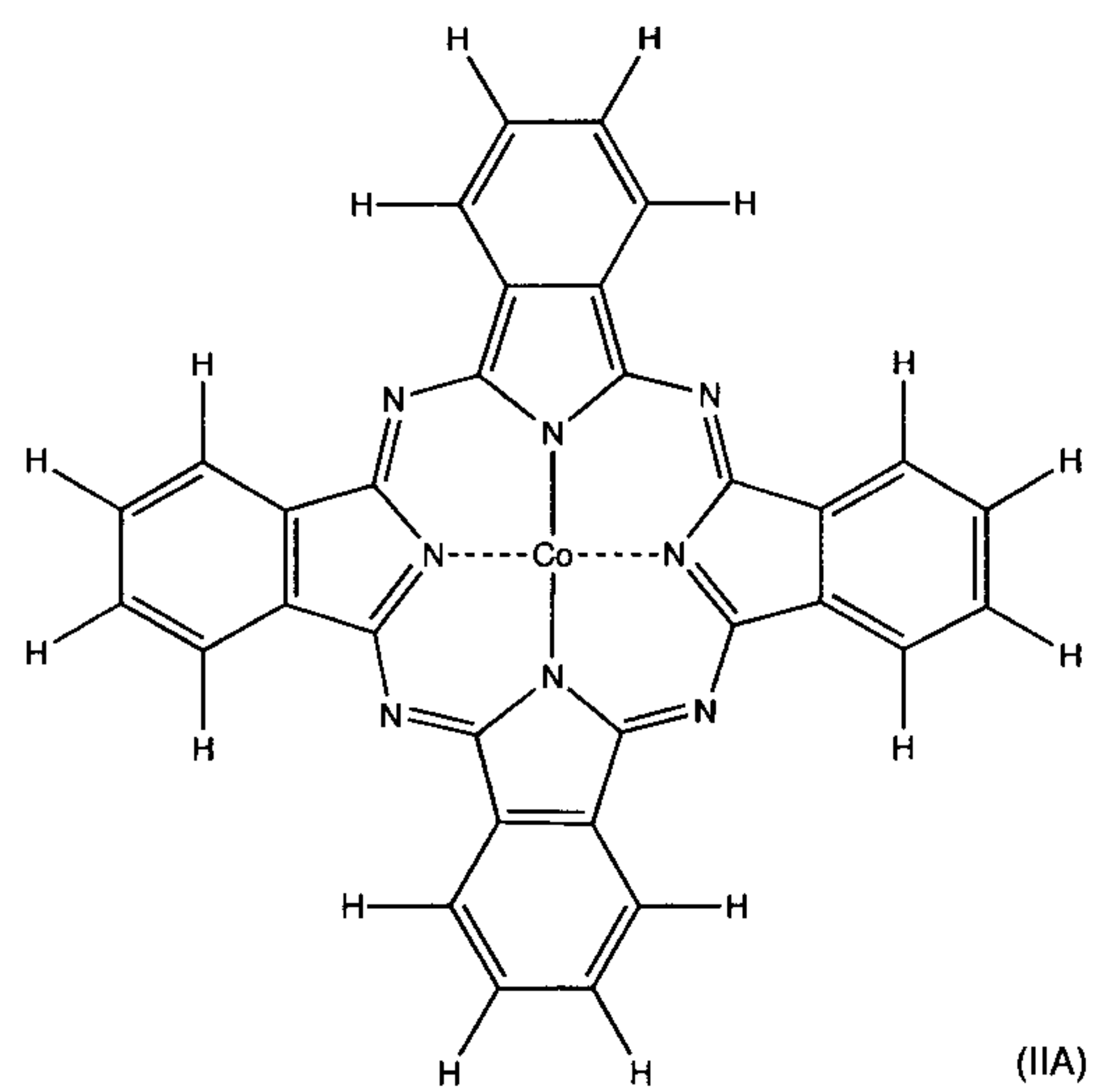
- wherein N is a nitrogen atom and M comprises a transition metal ligated by a tetraazamacrocycle.

5. The electrochemical carbon monoxide sensor according to claim 1, wherein the organometallic coordination complex comprises a compound of formula (II):

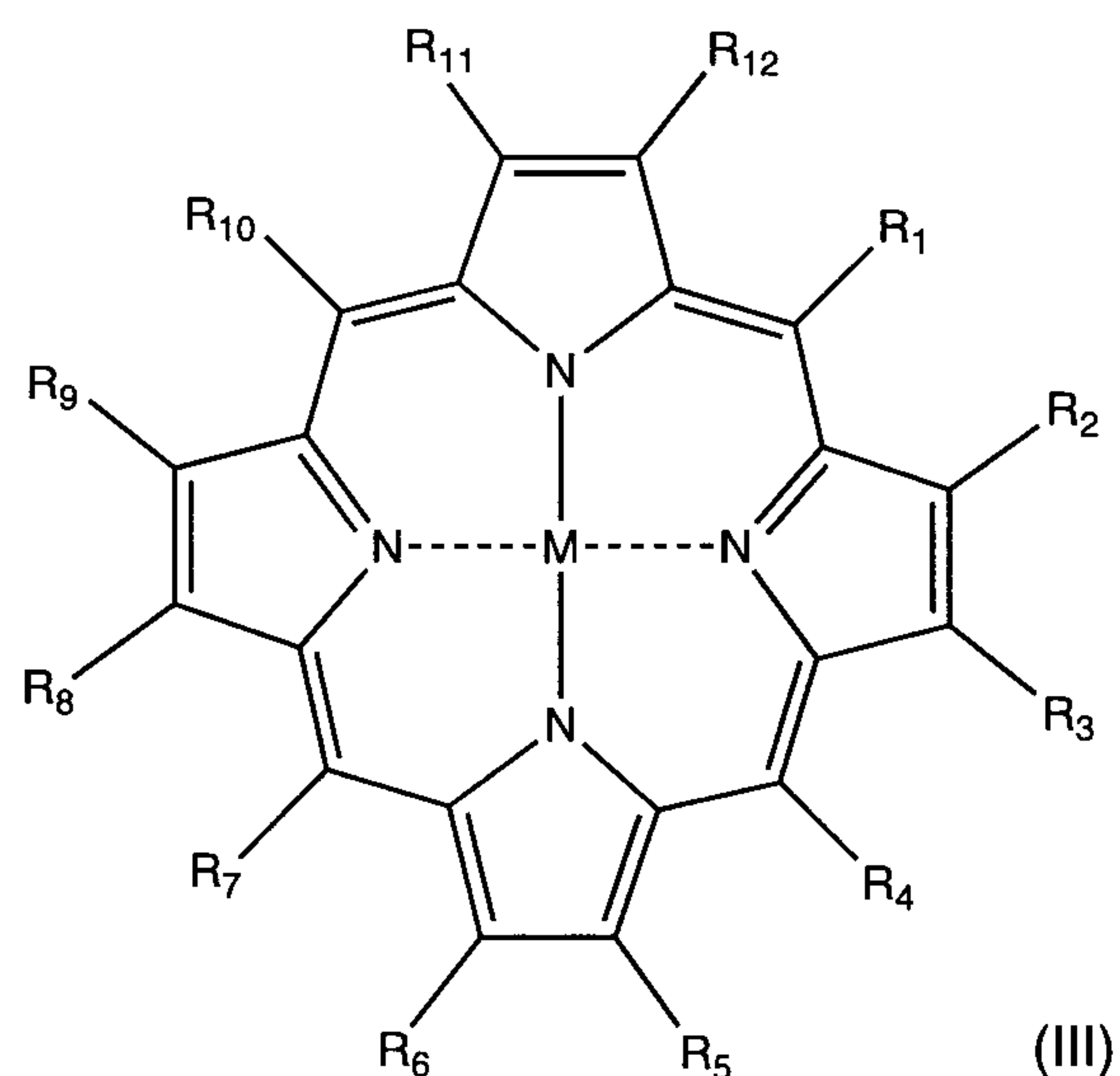


- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{16} are the same or different and comprise H, NO_2 , NH_2 , NHR_{17} , $\text{N}(\text{R}_{18})_2$, CO_2H , CO_2R_{19} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{20} , SH , SR_{21} , and combinations thereof; and wherein R_{17-21} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s).

6. The electrochemical carbon monoxide sensor according to claim 1, wherein the organometallic coordination complex comprises a compound of formula (IIA), (IIB), or (IIC):

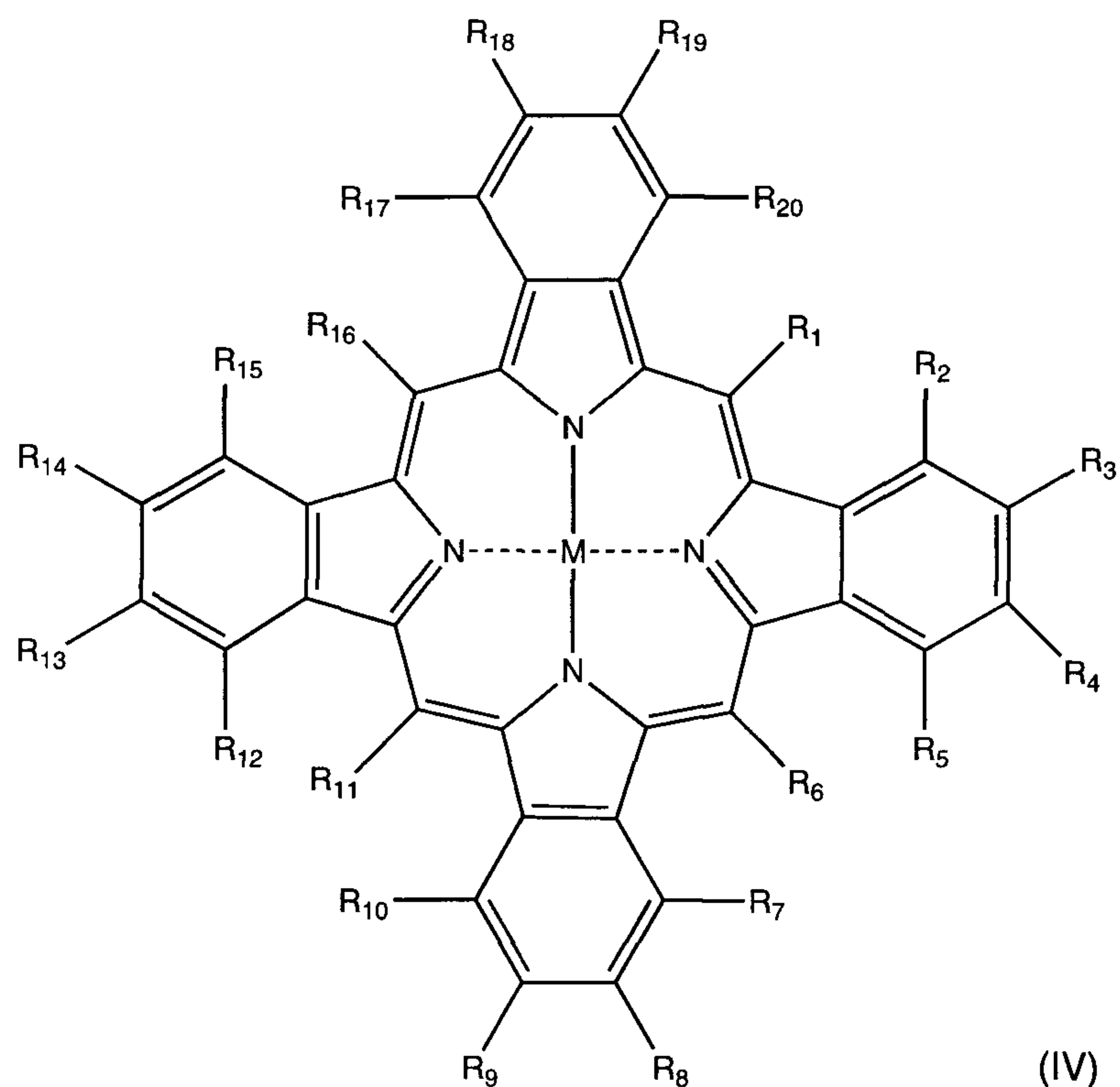


7. The electrochemical carbon monoxide sensor according to claim 1, wherein the organometallic coordination complex comprises a compound of formula (III):



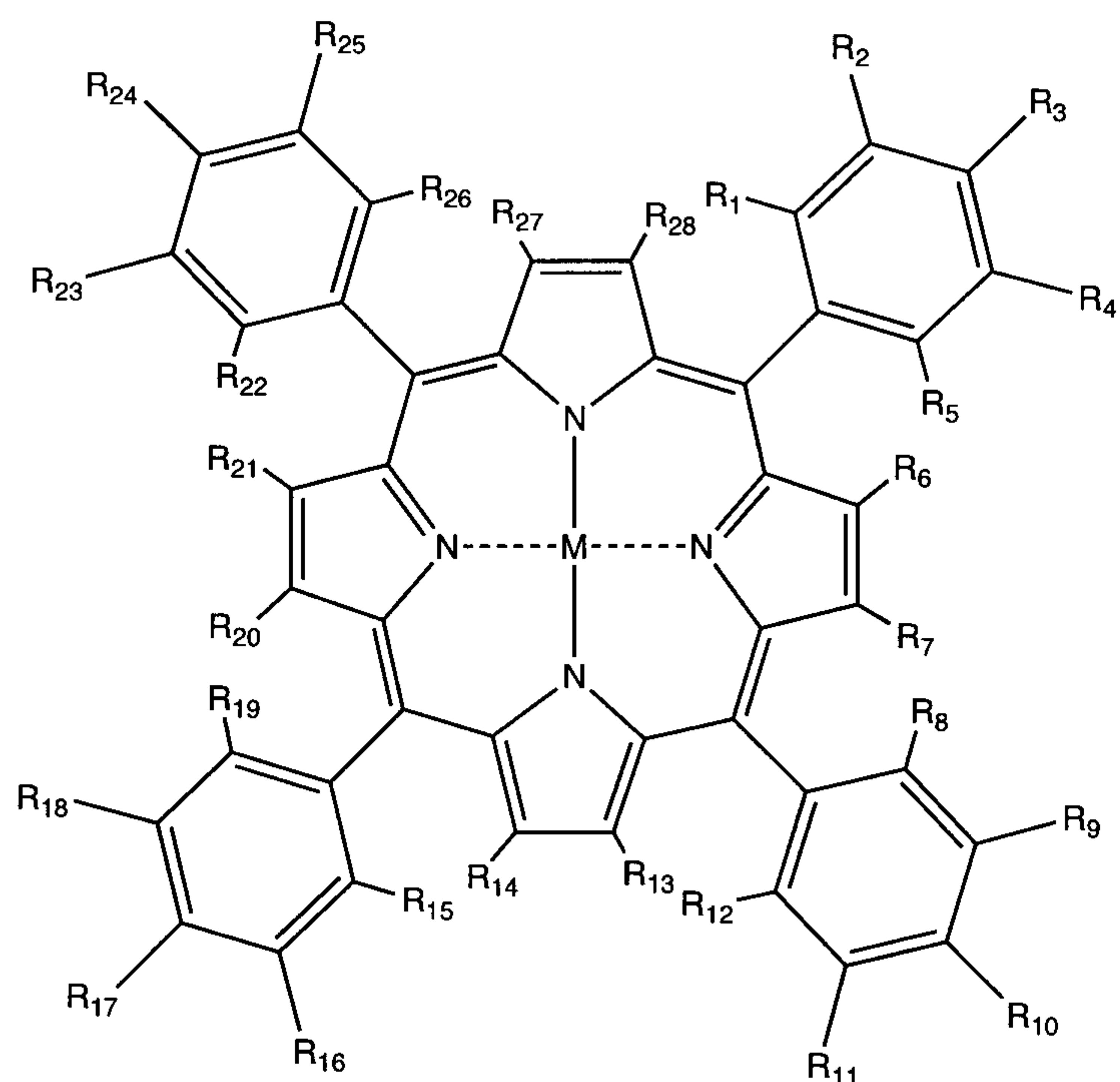
- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{12} are the same or different and comprise H, NO_2 , NH_2 , NHR_{13} , $\text{N(R}_{14})_2$, CO_2H , CO_2R_{15} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{16} , SH , SR_{17} , and combinations thereof; and wherein R_{13-17} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s).

8. The electrochemical carbon monoxide sensor according to claim 1, wherein the organometallic coordination complex comprises a compound of formula (IV):



- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{20} are the same or different and comprise H, NO_2 , NH_2 , NHR_{21} , $\text{N(R}_{22})_2$, CO_2H , CO_2R_{23} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{24} , SH , SR_{25} , and combinations thereof; and wherein R_{21-25} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s).

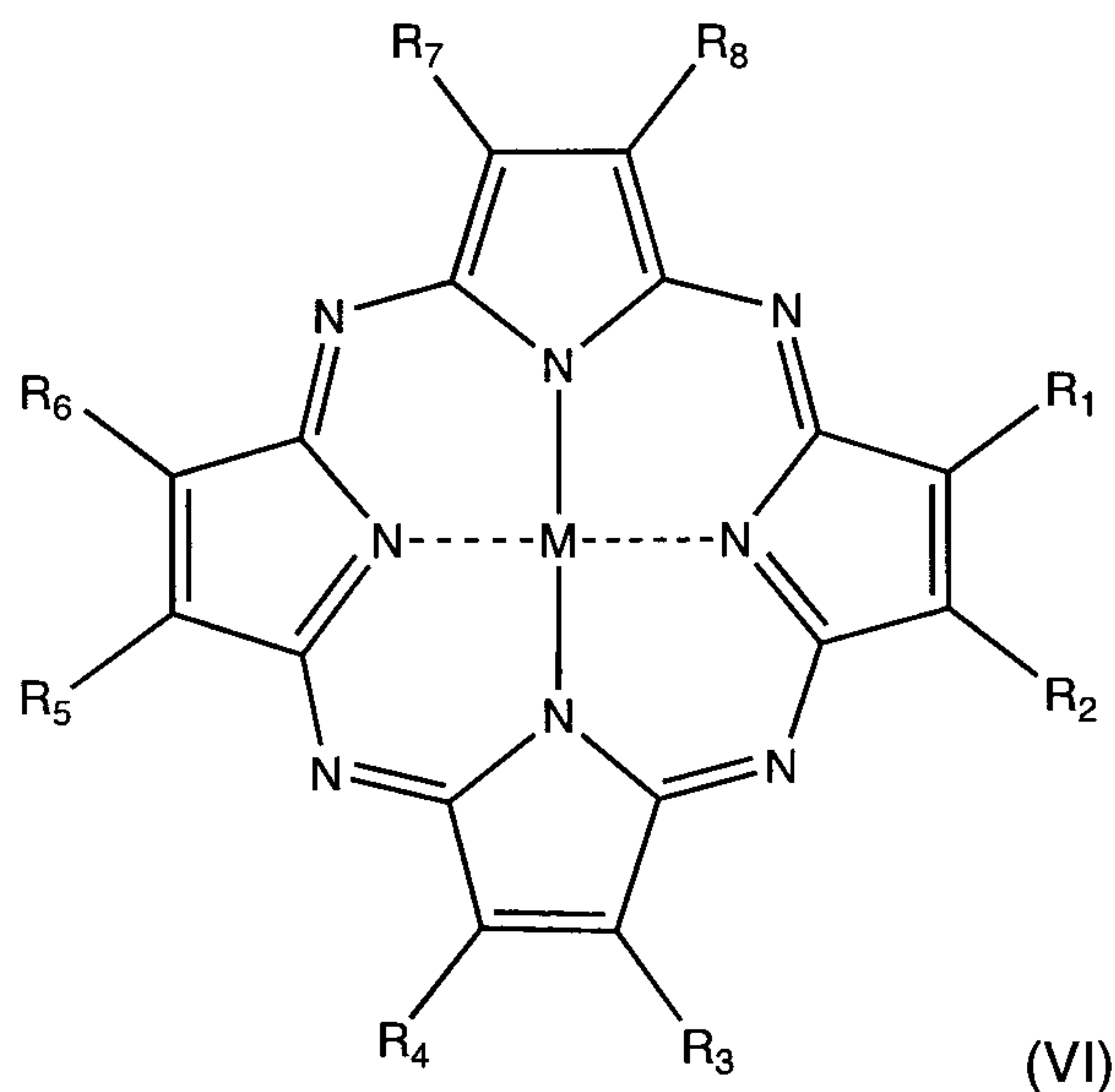
9. The electrochemical carbon monoxide sensor according to claim 1, wherein the organometallic coordination complex comprises a compound of formula (V):



(V)

- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{28} are the same or different and comprise H, NO_2 , NH_2 , NHR_{29} , $\text{N(R}_{30})_2$, CO_2H , CO_2R_{31} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{32} , SH , SR_{33} , and combinations thereof; and wherein R_{29-33} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s).

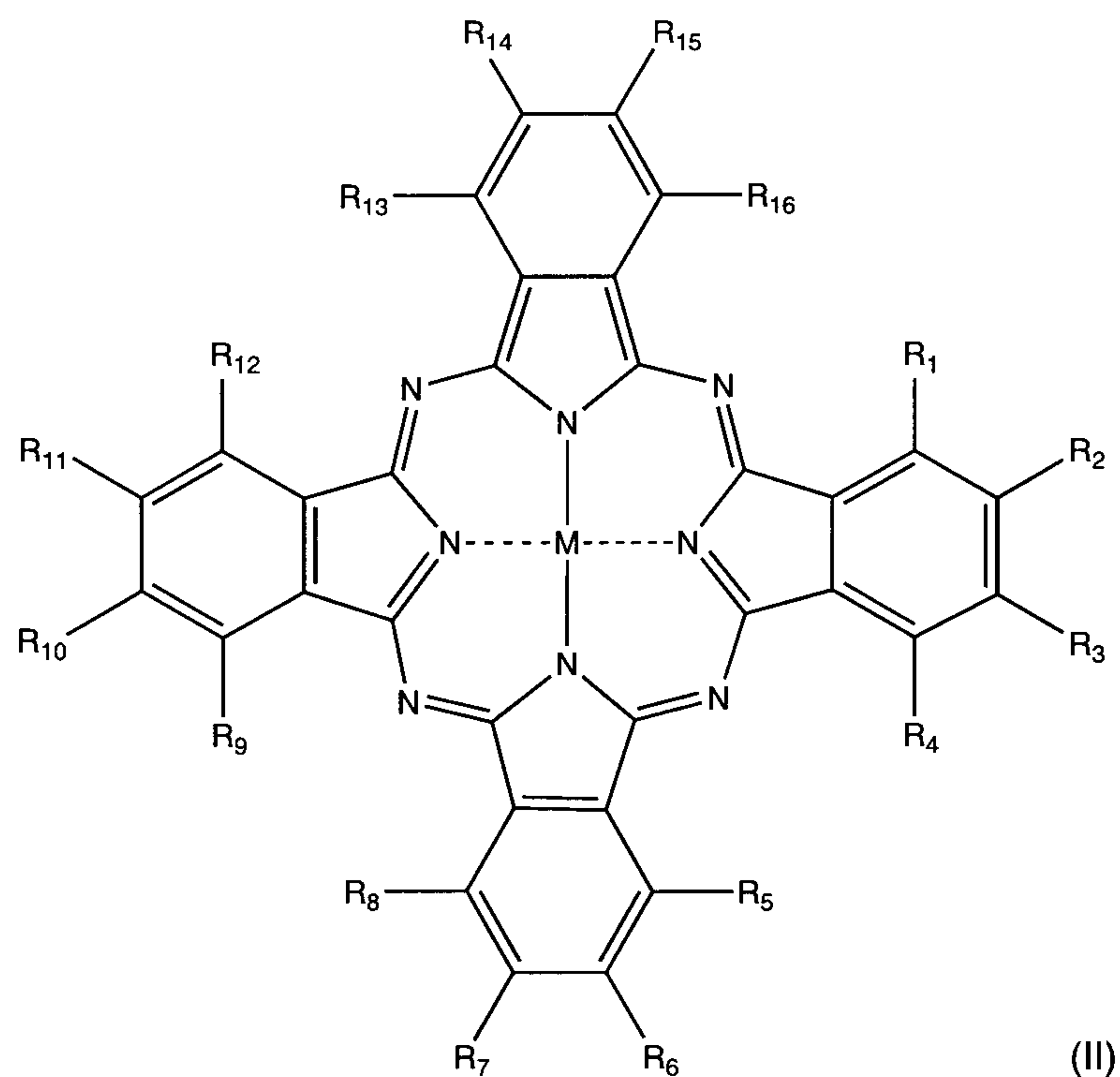
10. The electrochemical carbon monoxide sensor according to claim 1, wherein the organometallic coordination complex comprises a compound of formula (VI):



- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_8 are the same or different and comprise H, NO_2 , NH_2 , NHR_9 , $\text{N}(\text{R}_{10})_2$, CO_2H , CO_2R_{11} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{12} , SH , SR_{13} , and combinations thereof; and wherein R_9 - R_{13} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s).

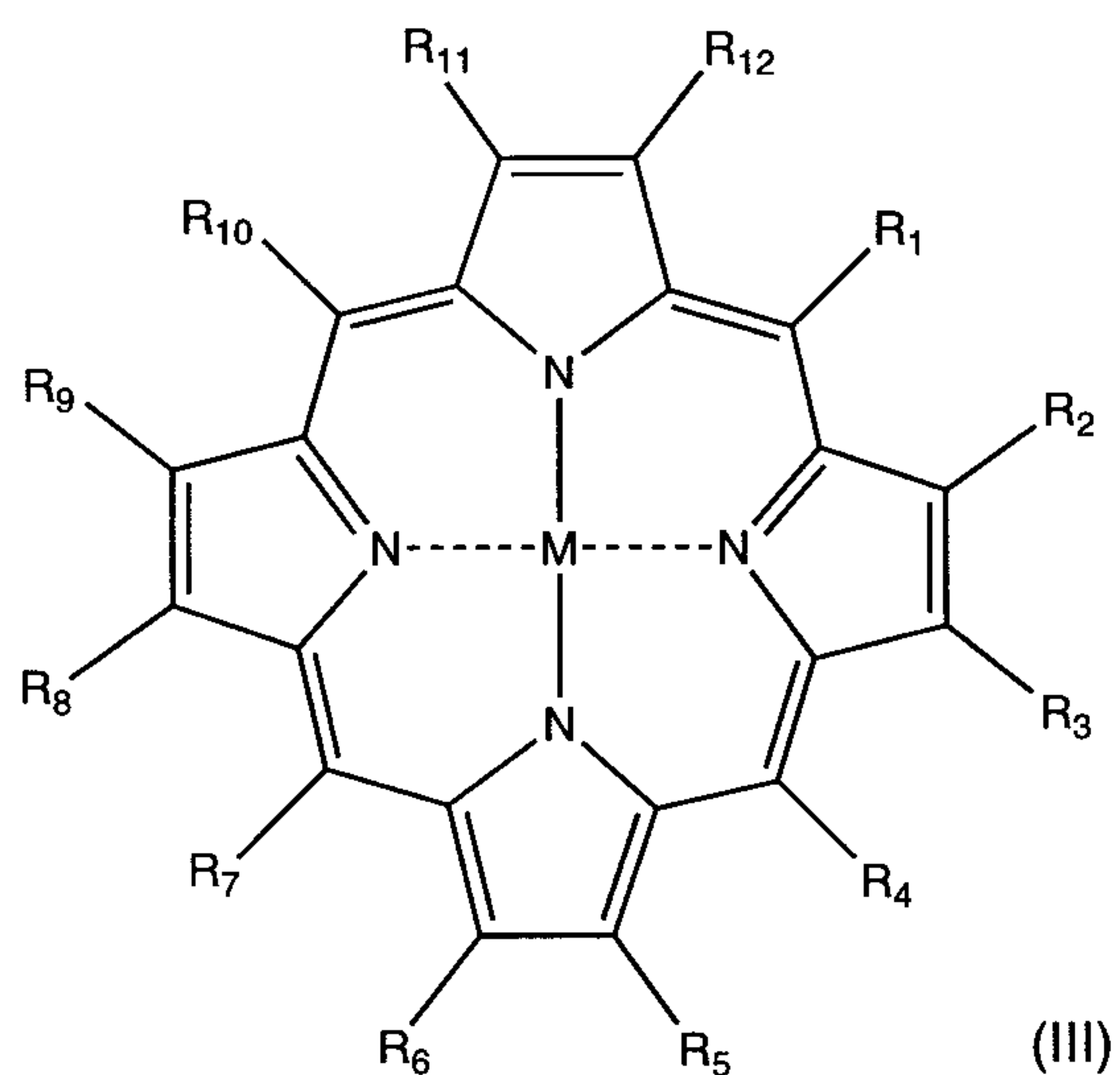
11. The electrochemical carbon monoxide sensor according to claim 1, wherein the organometallic coordination complex comprises a compound of formula (II), (III), (IV), (V), or (VI):

- wherein formula II is;



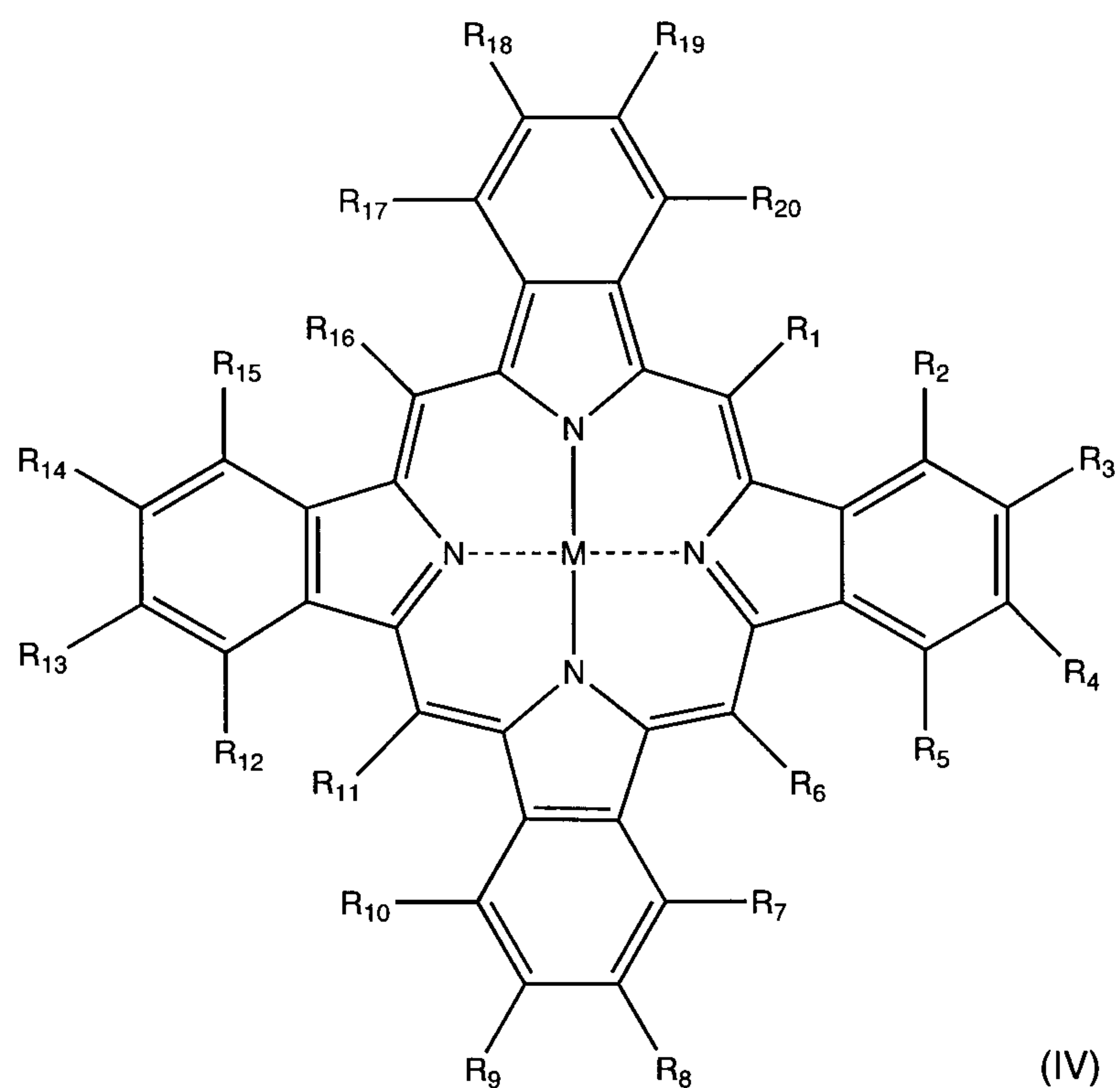
- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{16} are the same or different and comprise H, NO_2 , NH_2 , NHR_{17} , $\text{N(R}_{18})_2$, CO_2H , CO_2R_{19} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{20} , SH , SR_{21} , and combinations thereof; and wherein R_{17-21} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s);

- wherein formulate III is;



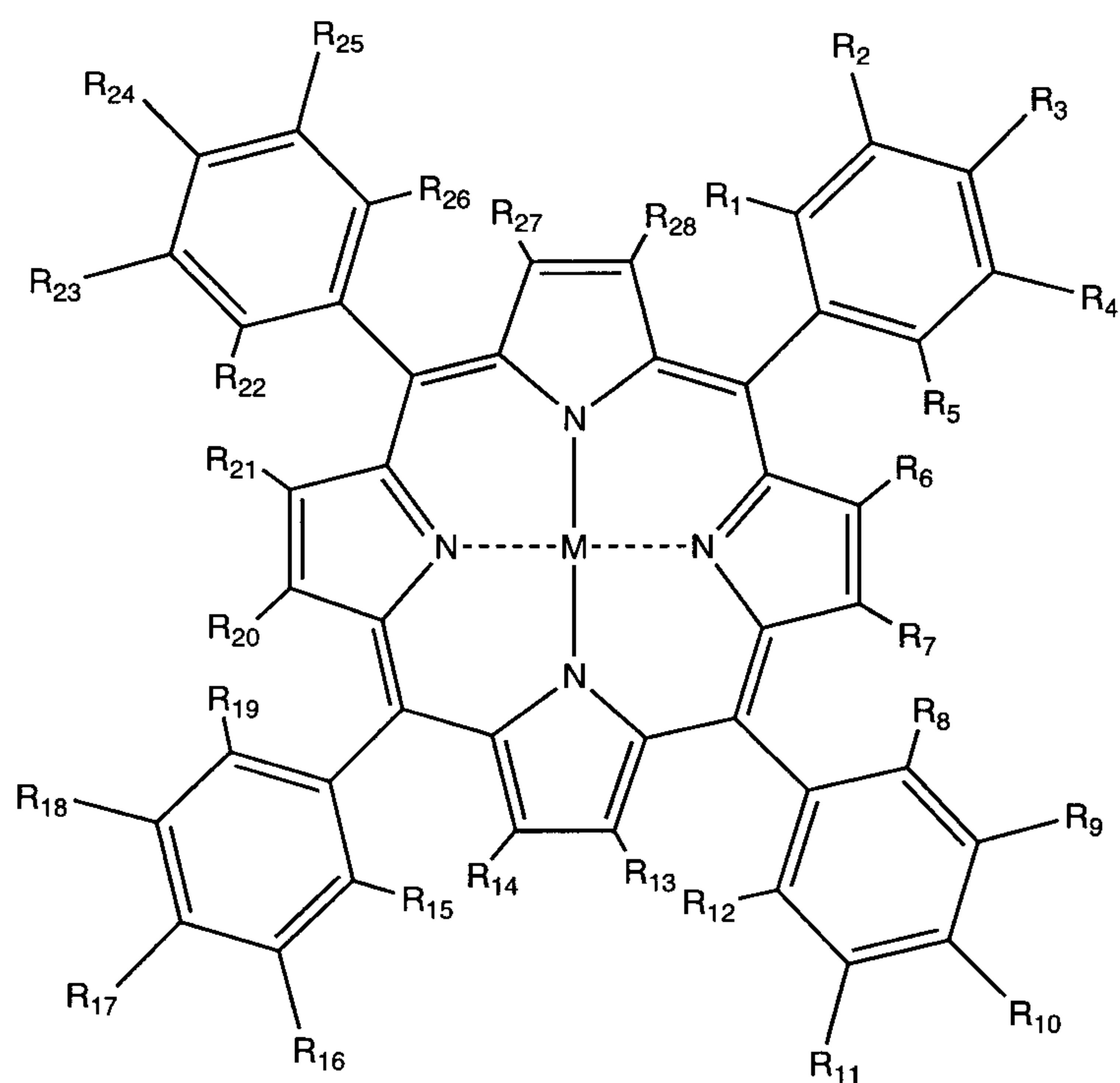
- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{12} are the same or different and comprise H, NO_2 , NH_2 , NHR_{13} , $\text{N}(\text{R}_{14})_2$, CO_2H , CO_2R_{15} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{16} , SH , SR_{17} , and combinations thereof; and wherein R_{13-17} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s);

- wherein formulate IV is;



- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{20} are the same or different and comprise H, NO_2 , NH_2 , NHR_{21} , $\text{N(R}_{22})_2$, CO_2H , CO_2R_{23} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{24} , SH , SR_{25} , and combinations thereof; and wherein R_{21-25} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s);

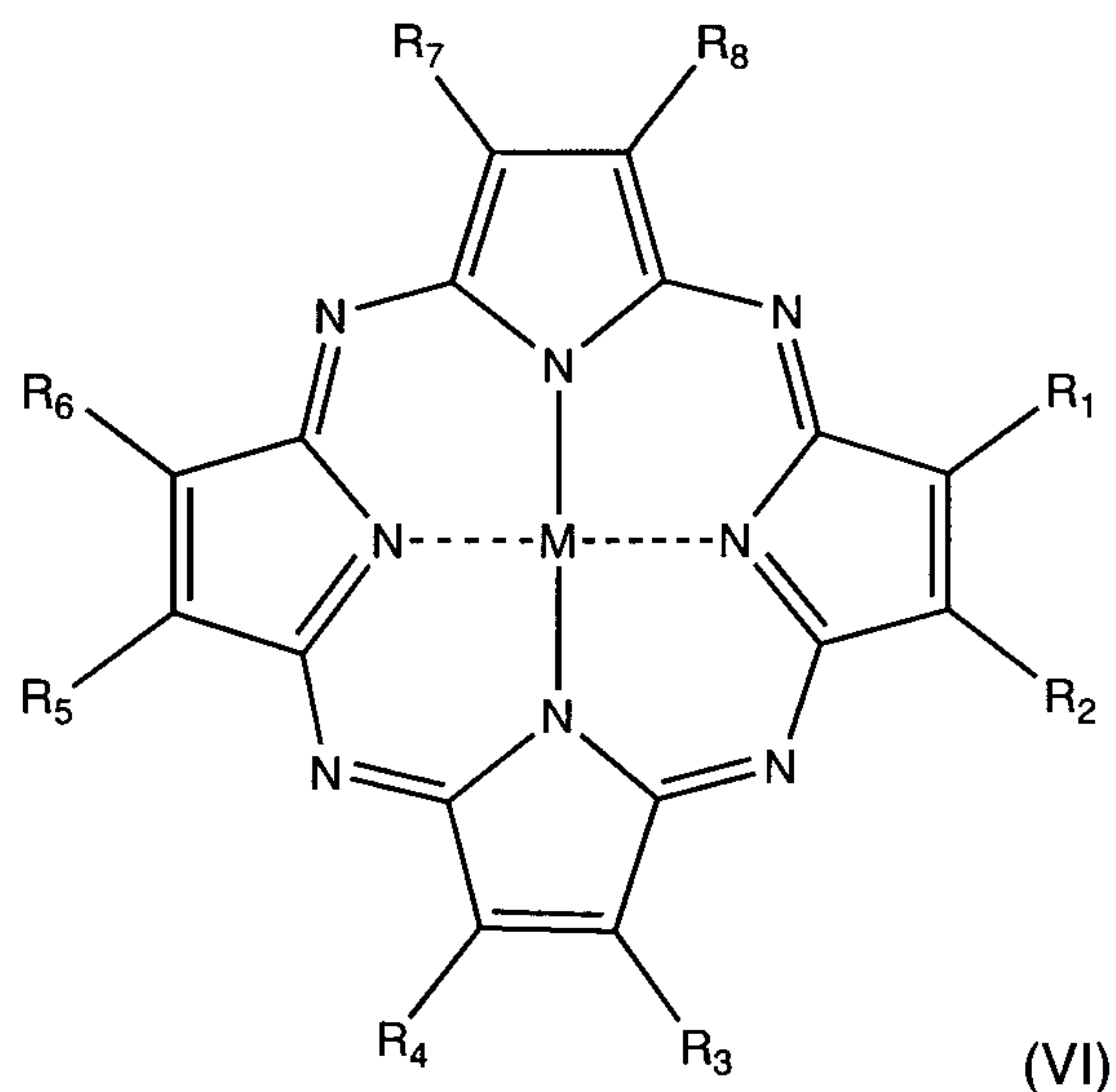
- wherein formulate V is;



(V)

- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{28} are the same or different and comprise H, NO_2 , NH_2 , NHR_{29} , $\text{N(R}_{30})_2$, CO_2H , CO_2R_{31} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{32} , SH, SR_{33} , and combinations thereof; and wherein R_{29-33} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s); and

- wherein formulate VI is:



- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_8 are the same or different and comprise H, NO_2 , NH_2 , NHR_9 , $\text{N}(\text{R}_{10})_2$, CO_2H , CO_2R_{11} , an alkyl group containing approximately 1 to approximately 10 carbon atom(s), OR_{12} , SH , SR_{13} , and combinations thereof; and wherein R_{9-13} are the same or different and comprise an alkyl group containing approximately 1 to approximately 10 carbon atom(s).

12. The electrochemical carbon monoxide sensor according to claim 1, wherein the carbonaceous material is selected from the group comprising graphene, graphite, amorphous carbon, carbon nanotubes, carbon fibers, and combinations thereof.

13. The electrochemical carbon monoxide sensor according to claim 1, further comprising a desiccant for retaining a liquid.

14. An electrochemical carbon monoxide sensor for use in a gas/fire detector, said electrochemical carbon monoxide sensor being exposed to a sample gas during normal sensing operation, comprising:

- a housing, wherein the housing comprises a sidewall, a top wall, and a bottom wall, and wherein the sidewall, the top wall and the bottom wall define a containment region for containing a micro electrode assembly therein, and further wherein the top wall of the housing comprises a gaseous diffusion aperture;

- wherein the micro electrode assembly comprises an anode, a cathode and an ion conducting membrane, and wherein the anode and the cathode are discrete elements, and

wherein the ion conducting membrane permits ion transport between the anode and the cathode, and wherein the ion conducting membrane prevents electron conduction between the anode and the cathode;

- wherein the cathode comprises an oxygen reduction catalyst that comprises a pyrolysis product of a carbonaceous material and an organometallic coordination complex of a transition metal with a nitrogen containing macrocycle that has been deposited on the carbonaceous material;

- wherein the oxygen reduction catalyst does not materially exhibit catalytic activity for the oxidation of carbon monoxide; and

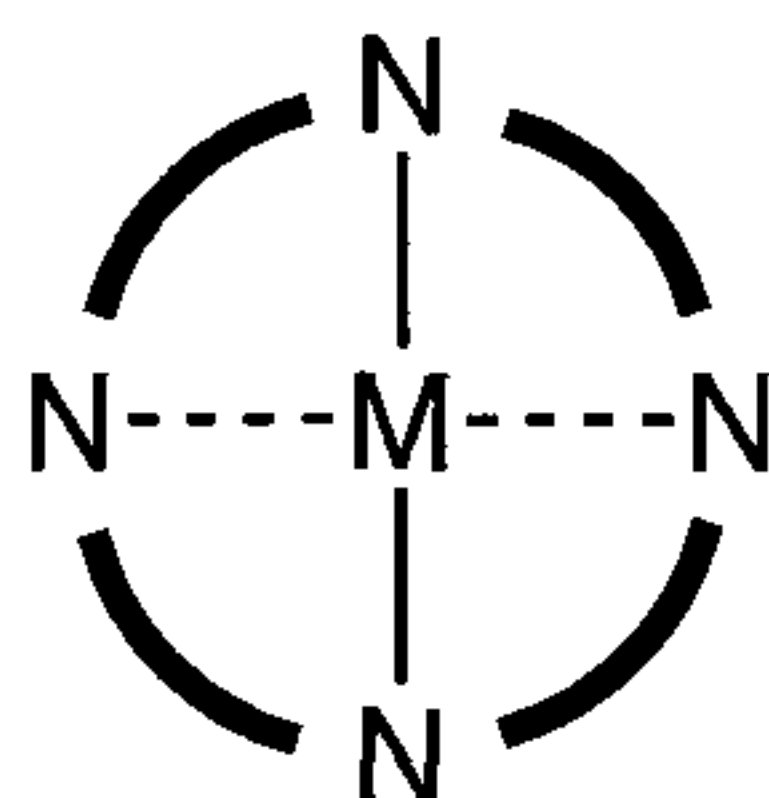
- wherein the anode and the cathode are configured to be exposed to the same sample gas during normal sensing operation.

15. The electrochemical carbon monoxide sensor according to claim 14, wherein the organometallic coordination complex comprises at least one of the group comprising substituted transition metal porphyrins, unsubstituted transition metal porphyrins, substituted transition metal tetrabenzoporphyrins, unsubstituted transition metal tetrabenzoporphyrins, substituted transition metal tetraphenylporphyrins, unsubstituted transition metal tetraphenylporphyrins, substituted transition metal tetraazaporphyrins, unsubstituted transition metal tetraazaporphyrins, substituted transition metal tetraazamacrocycles, unsubstituted transition metal tetraazamacrocycles, substituted transition metal phthalocyanines, unsubstituted transition metal phthalocyanines, substituted transition metal naphthalocyanines, unsubstituted transition metal naphthalocyanines, substituted transition metal bis(phthalocyanines), unsubstituted transition metal bis(phthalocyanines), substituted transition metal bis(naphthalocyanines), unsubstituted transition metal bis(naphthalocyanines), or combinations thereof.

16. The electrochemical carbon monoxide sensor according to claim 14, wherein the organometallic coordination complex comprises at least one of the group comprising substituted cobalt porphyrins, unsubstituted cobalt porphyrins, substituted cobalt tetrabenzoporphyrins, unsubstituted cobalt tetrabenzoporphyrins, substituted cobalt tetraphenylporphyrins, unsubstituted cobalt tetraphenylporphyrins, substituted cobalt tetraazaporphyrins, unsubstituted cobalt tetraazaporphyrins, substituted cobalt tetraazamacrocycles, unsubstituted cobalt tetraazamacrocycles, substituted cobalt metal phthalocyanines, unsubstituted cobalt phthalocyanines, substituted cobalt

naphthalocyanines, unsubstituted cobalt naphthalocyanines, substituted cobalt bis(phthalocyanines), unsubstituted cobalt bis(phthalocyanines), substituted cobalt bis(naphthalocyanines), unsubstituted cobalt bis(naphthalocyanines), or combinations thereof.

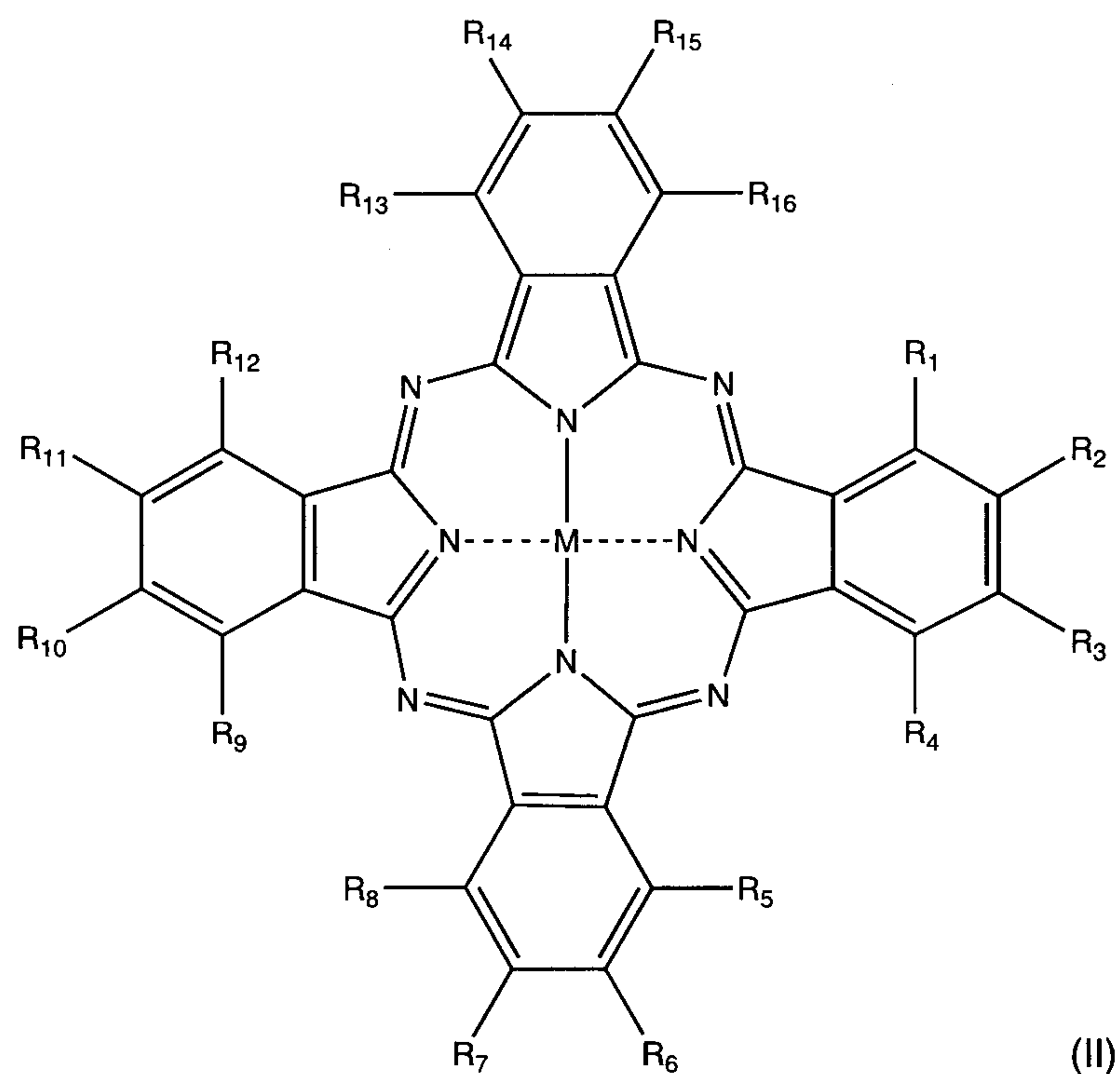
17. The electrochemical carbon monoxide sensor according to claim 14, wherein the organometallic coordination complex comprises a compound of formula (I):



(I)

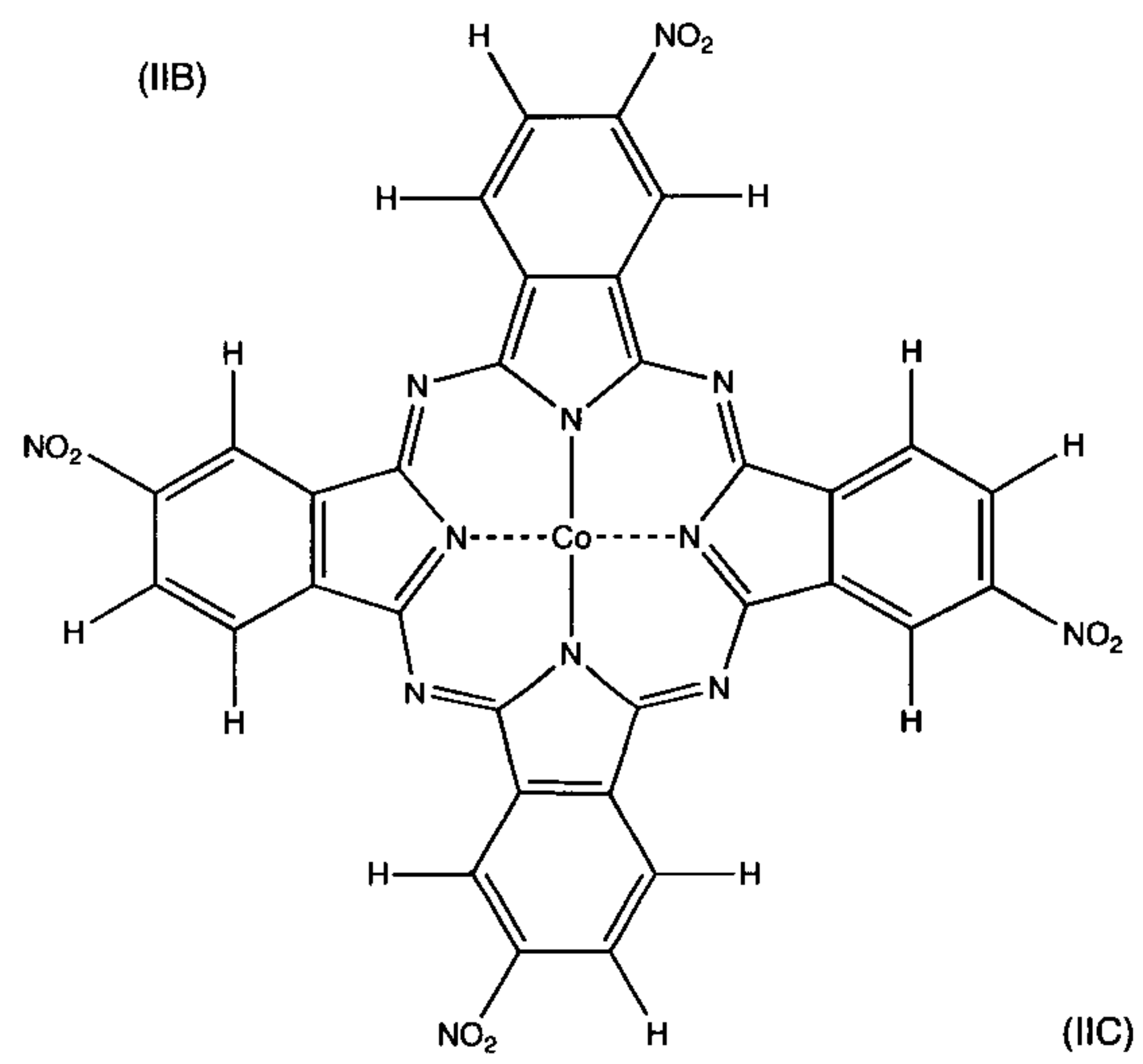
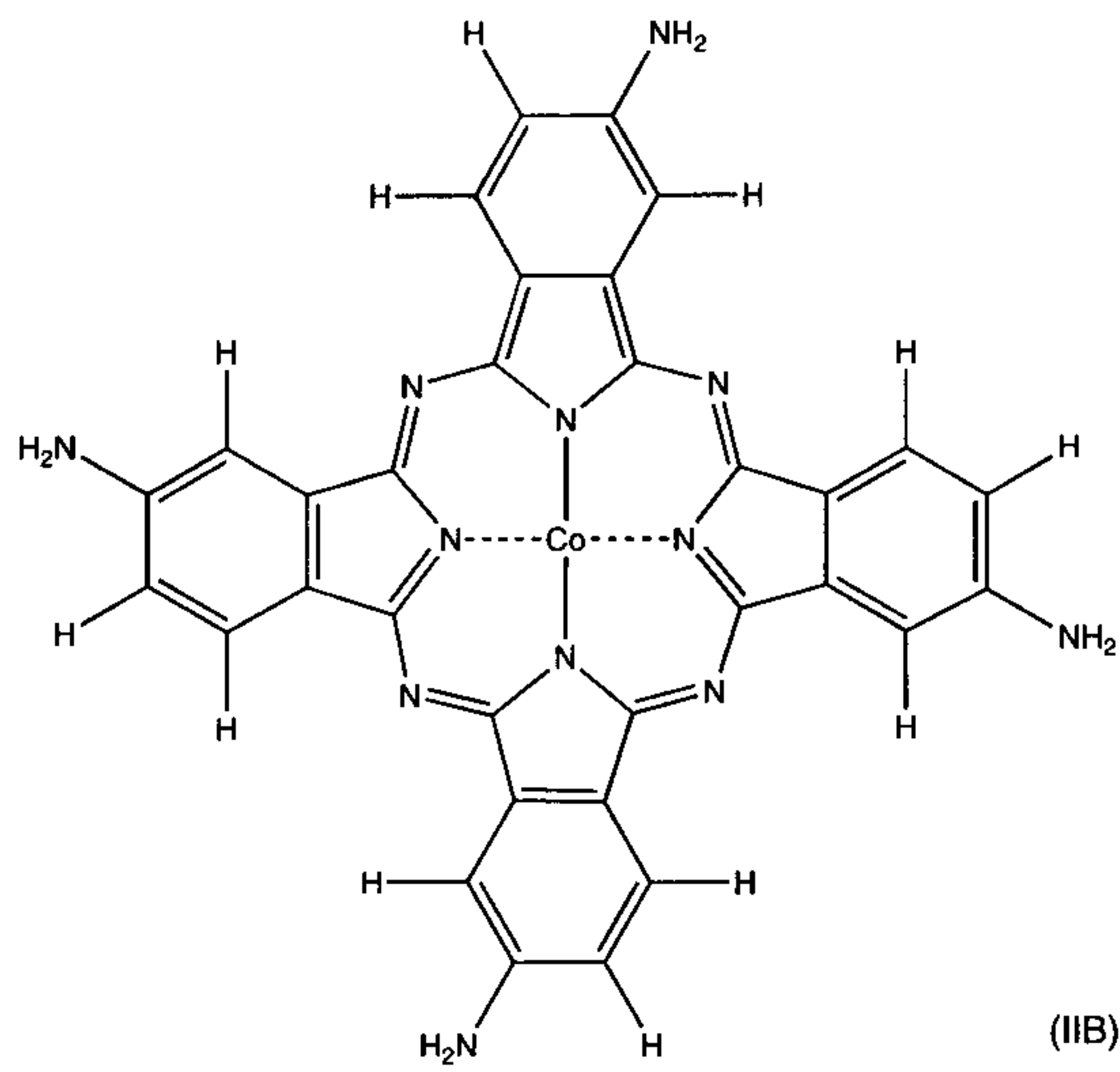
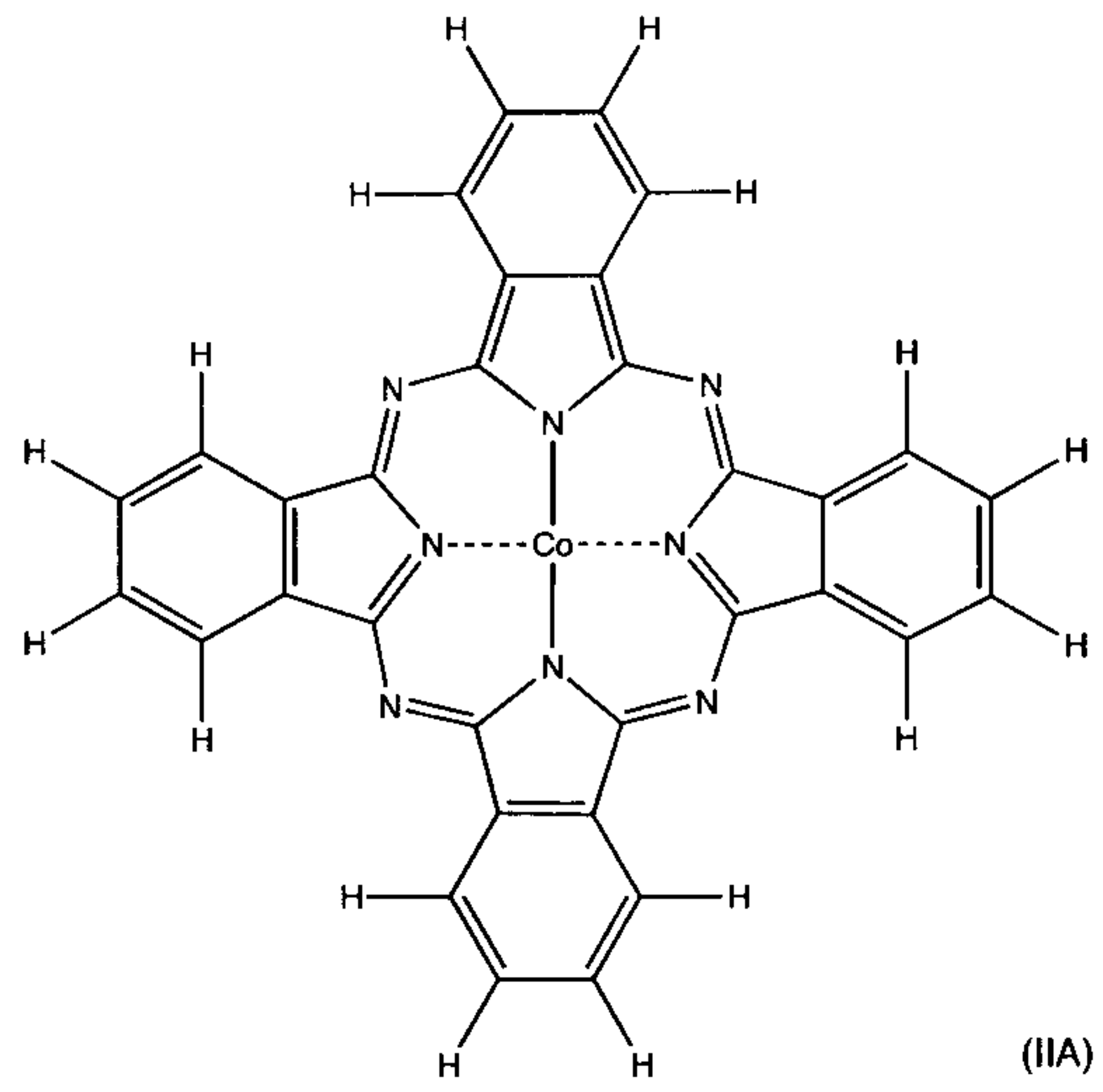
- wherein N is a nitrogen atom and M comprises a transition metal ligated by a tetraazamacrocyclic.

18. The electrochemical carbon monoxide sensor according to claim 14, wherein the organometallic coordination complex comprises a compound of formula (II):

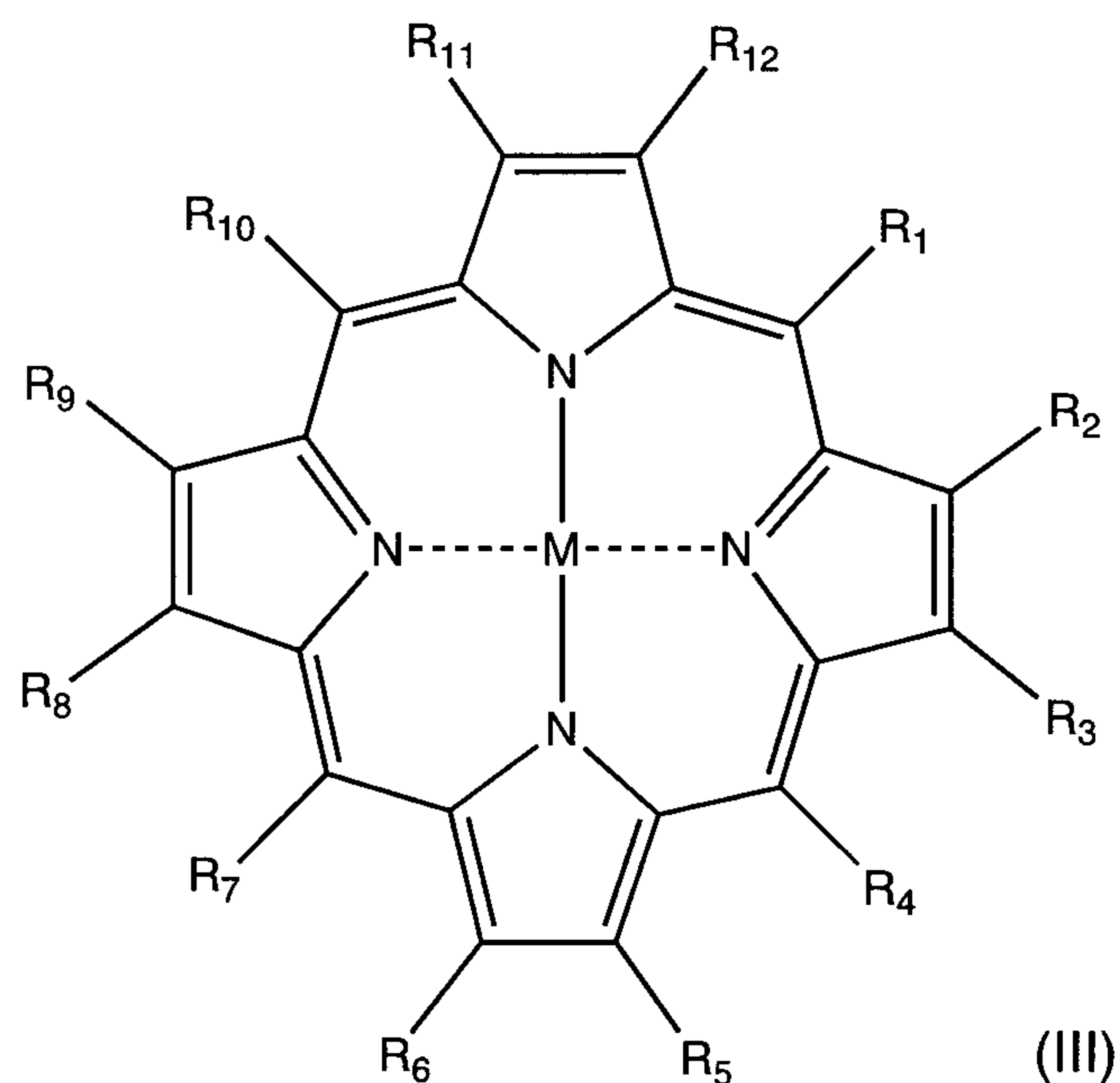


- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R₁-R₁₆ are the same or different and comprise H, NO₂, NH₂, an amine, CO₂H, an ester, an alkyl group containing approximately 1 to approximately 10 carbon atom(s), an ether, SH, a thioether, or combinations thereof.

19. The electrochemical carbon monoxide sensor according to claim 14, wherein the organometallic coordination complex comprises a compound of formula (IIA), (IIB), or (IIC):

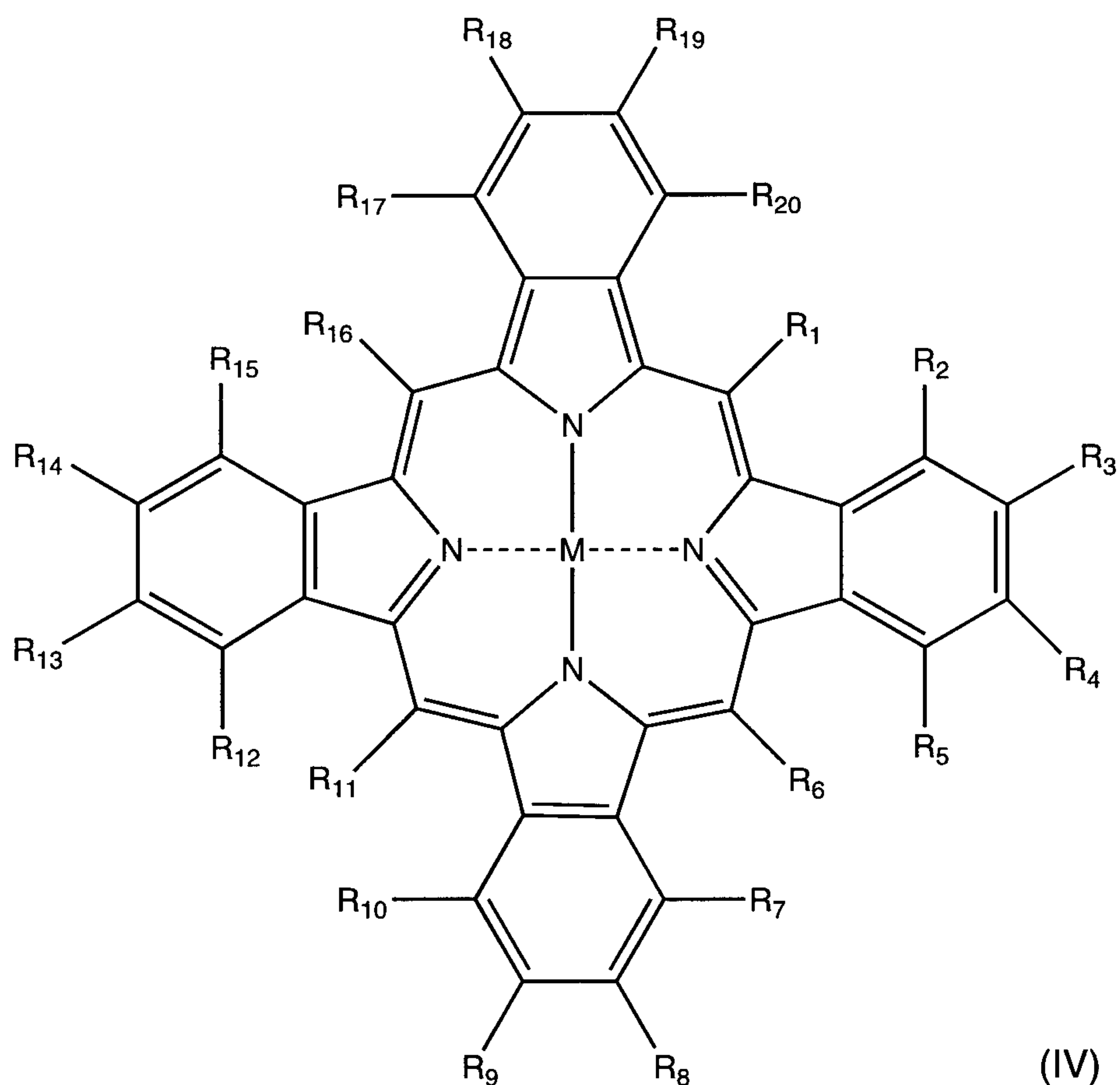


20. The electrochemical carbon monoxide sensor according to claim 14, wherein the organometallic coordination complex comprises a compound of formula (III):



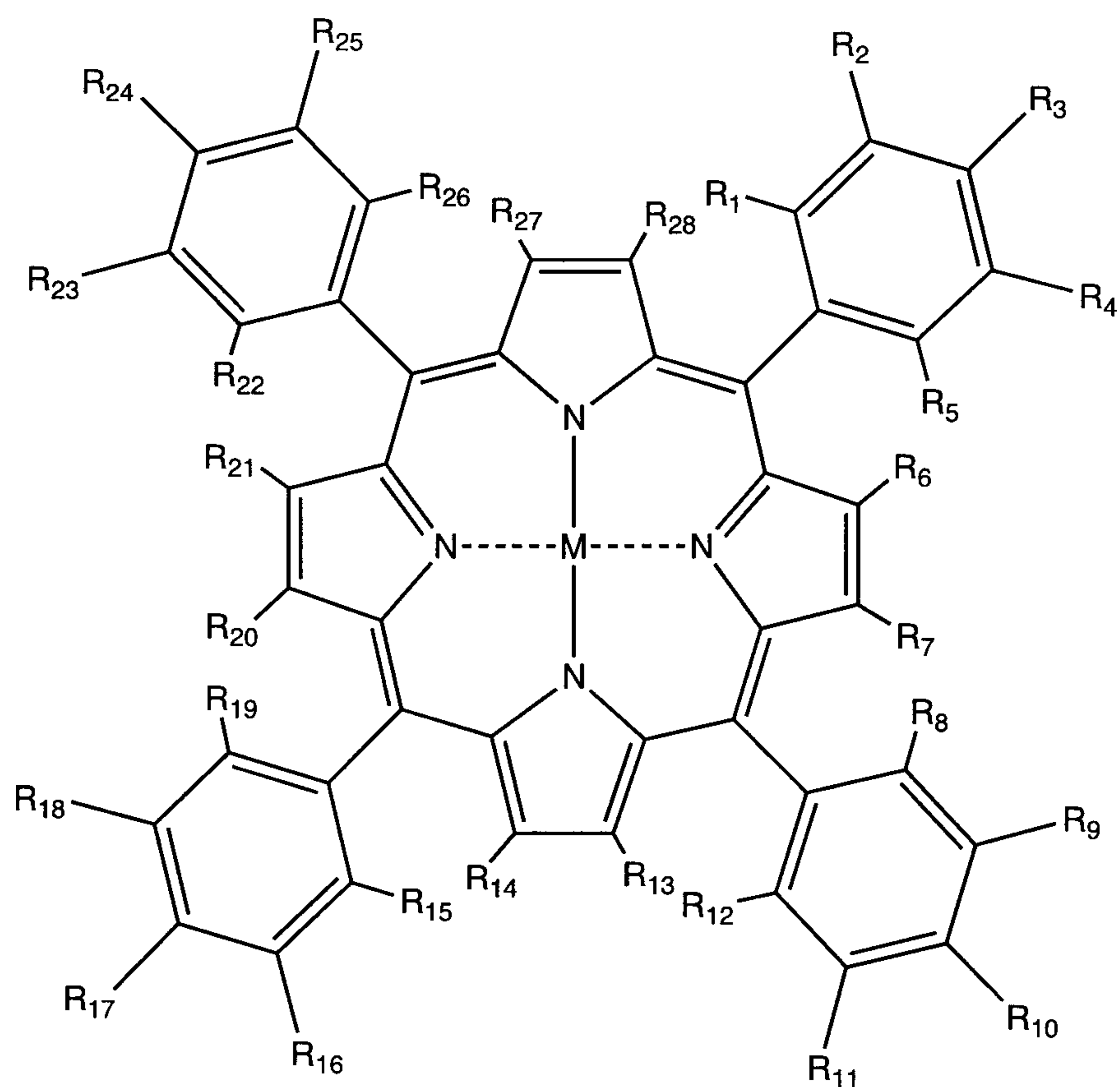
- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{12} are the same or different and comprise H, NO_2 , NH_2 , an amine, CO_2H , an ester, an alkyl group containing approximately 1 to approximately 10 carbon atom(s), an ether, SH, a thioether, or combinations thereof.

21. The electrochemical carbon monoxide sensor according to claim 14, wherein the organometallic coordination complex comprises a compound of formula (IV):



- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R₁-R₂₀ are the same or different and comprise H, NO₂, NH₂, an amine, CO₂H, an ester, an alkyl group containing approximately 1 to approximately 10 carbon atom(s), an ether, SH, a thioether, or combinations thereof.

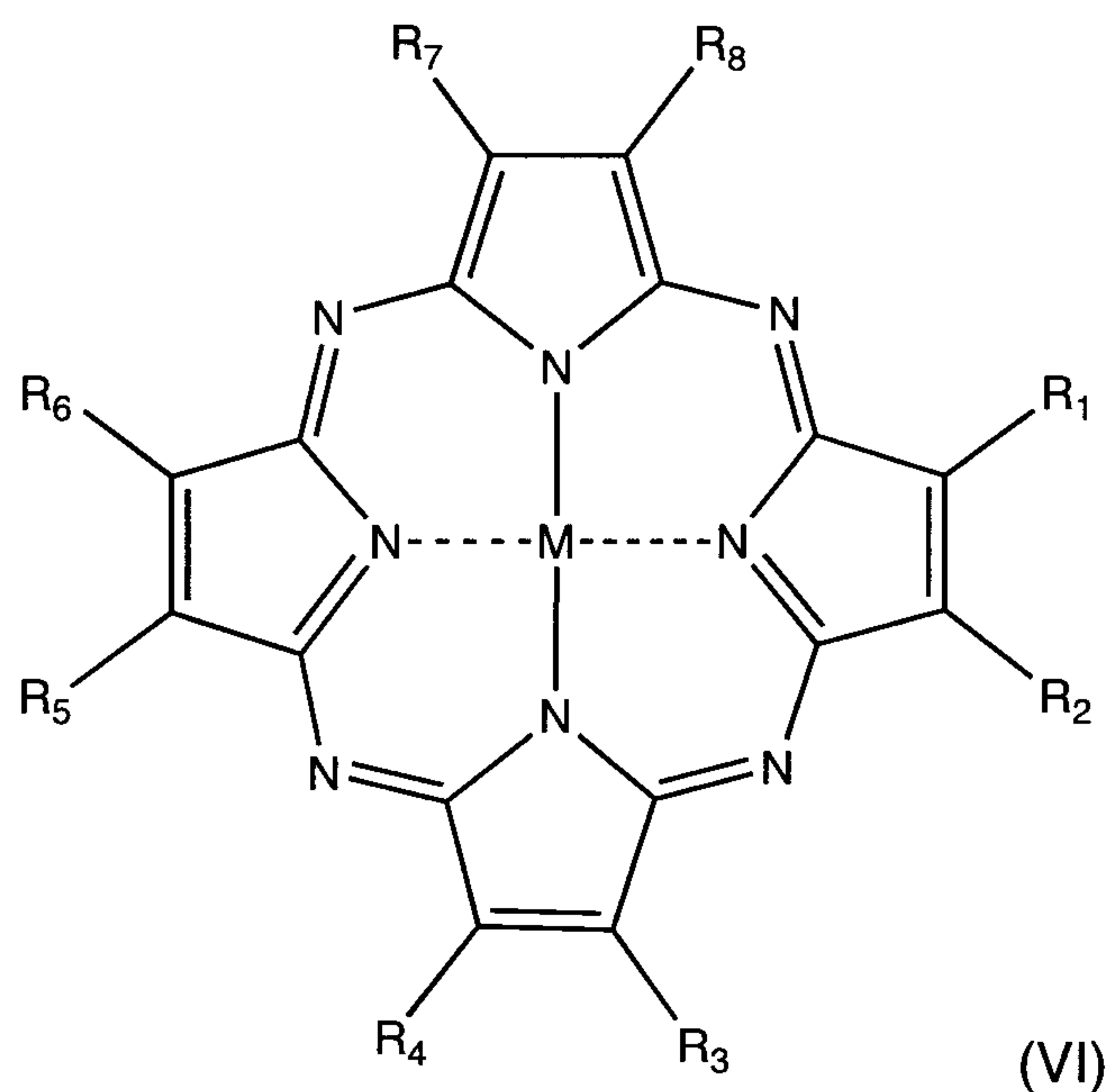
22. The electrochemical carbon monoxide sensor according to claim 14, wherein the organometallic coordination complex comprises a compound of formula (V):



(V)

- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{28} are the same or different and comprise H, NO_2 , NH_2 , an amine, CO_2H , an ester, an alkyl group containing approximately 1 to approximately 10 carbon atom(s), an ether, SH, a thioether, or combinations thereof.

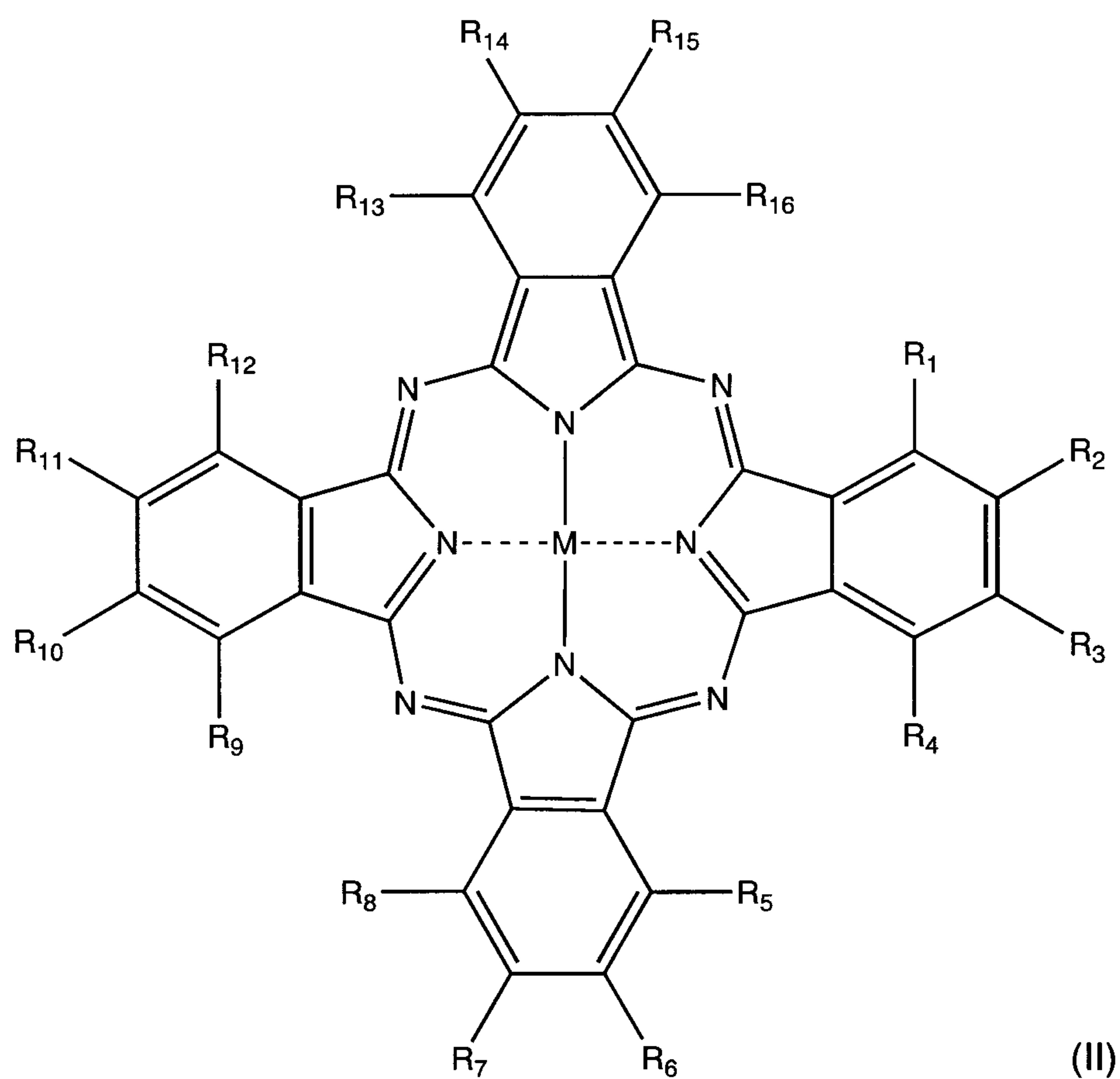
23. The electrochemical carbon monoxide sensor according to claim 14, wherein the organometallic coordination complex comprises a compound of formula (VI):



- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_8 are the same or different and comprise H, NO_2 , NH_2 , an amine, CO_2H , an ester, an alkyl group containing approximately 1 to approximately 10 carbon atom(s), an ether, SH, a thioether, or combinations thereof.

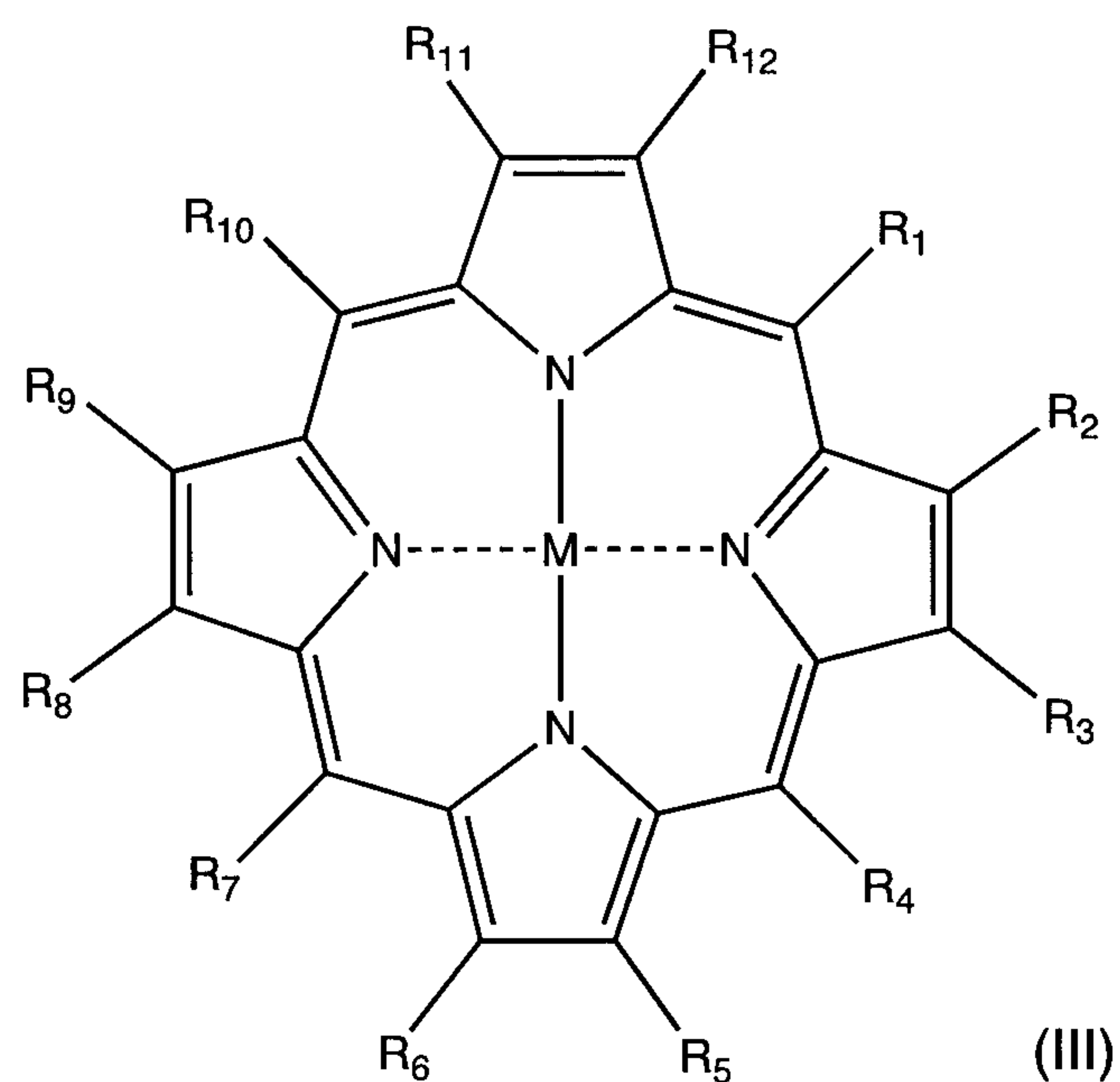
24. The electrochemical carbon monoxide sensor according to claim 14, wherein the organometallic coordination complex comprises a compound of formula (II), (III), (IV), (V), or (VI):

- wherein formula II is;



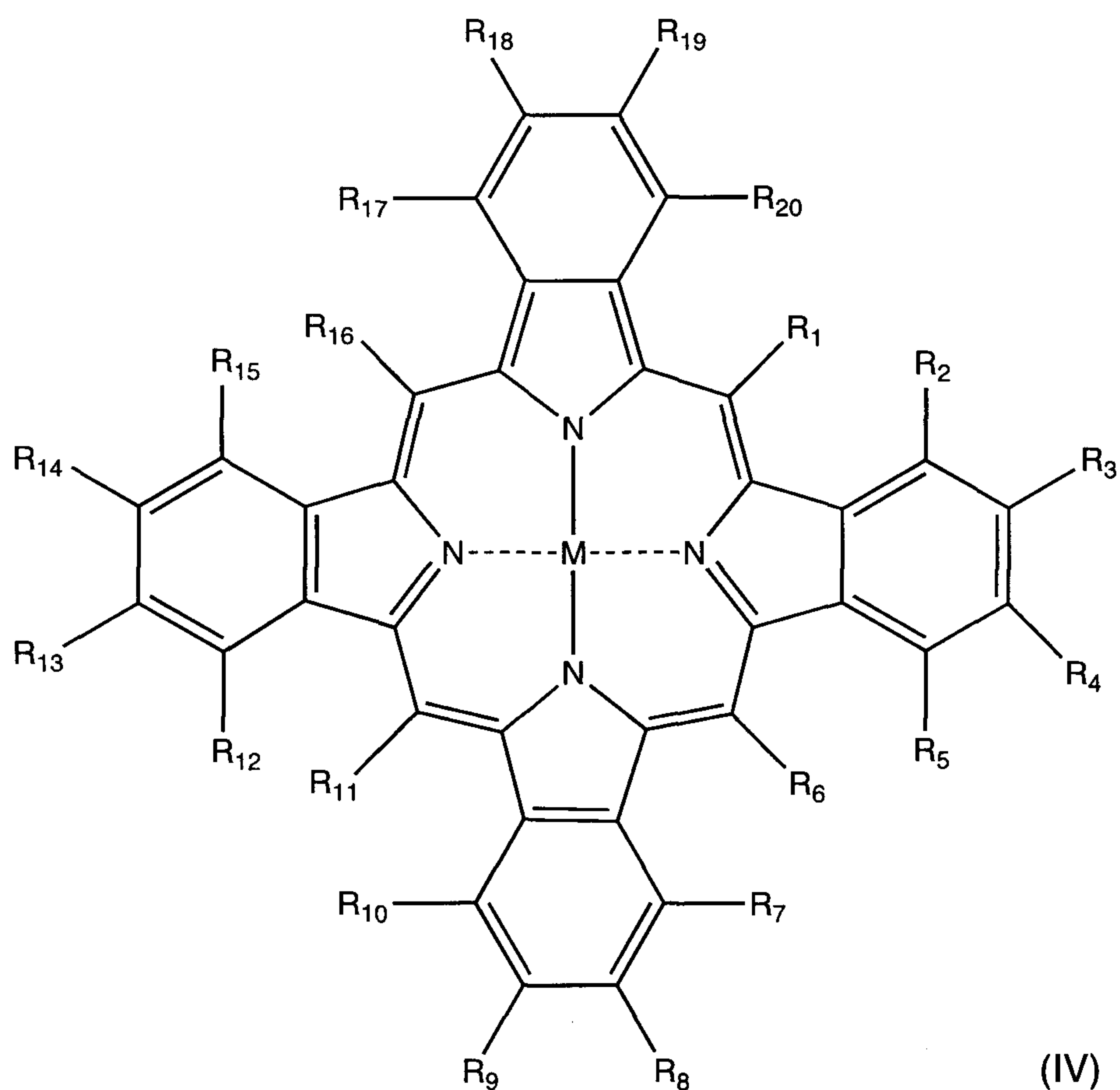
- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R₁-R₁₆ are the same or different and comprise H, NO₂, NH₂, an amine, CO₂H, an ester, an alkyl group containing approximately 1 to approximately 10 carbon atom(s), an ether, SH, a thioether, or combinations thereof;

- wherein formula III is;



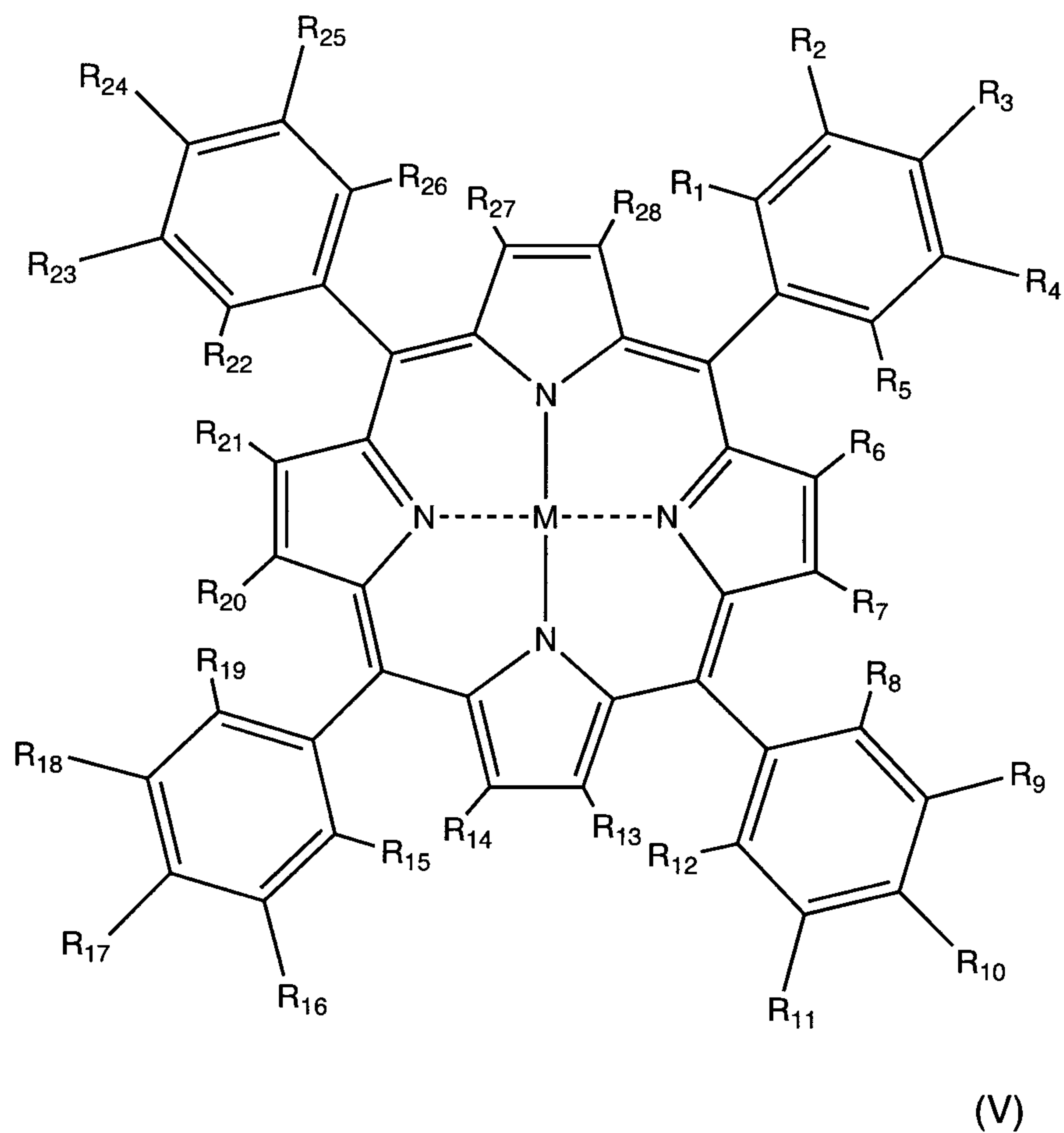
- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R₁-R₁₂ are the same or different and comprise H, NO₂, NH₂, an amine, CO₂H, an ester, an alkyl group containing approximately 1 to approximately 10 carbon atom(s), an ether, SH, a thioether, or combinations thereof;

- wherein formula IV is;



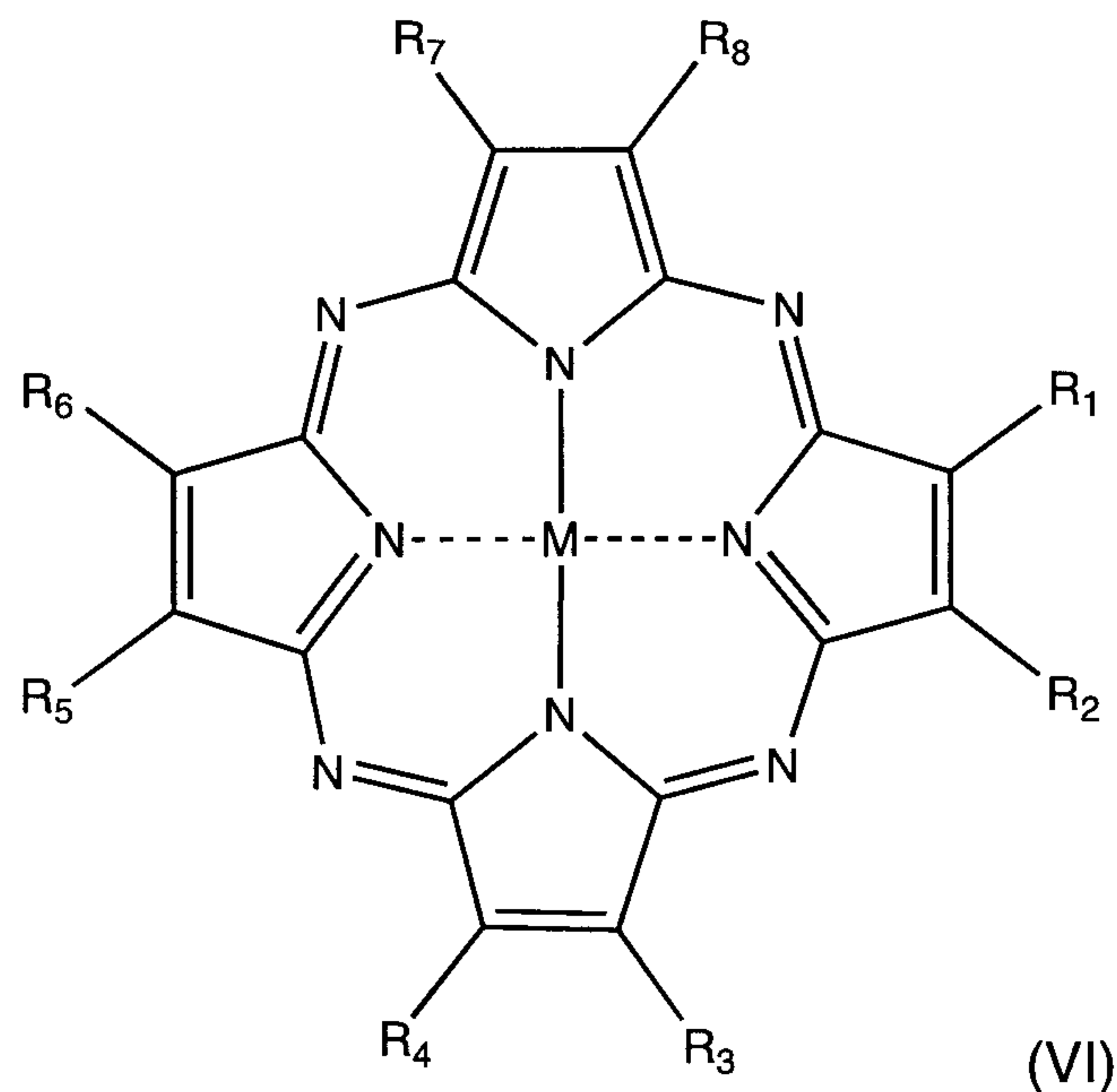
- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_{20} are the same or different and comprise H, NO_2 , NH_2 , an amine, CO_2H , an ester, an alkyl group containing approximately 1 to approximately 10 carbon atom(s), an ether, SH, a thioether, or combinations thereof;

- wherein formula V is;



- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R₁-R₂₈ are the same or different and comprise H, NO₂, NH₂, an amine, CO₂H, an ester, an alkyl group containing approximately 1 to approximately 10 carbon atom(s), an ether, SH, a thioether, or combinations thereof; and

- wherein formula VI is:



- wherein M comprises Co, Cu, Fe, Ir, Ni, Pd, Rh, Ru, or Zn; wherein R_1 - R_8 are the same or different and comprise H, NO_2 , NH_2 , an amine, CO_2H , an ester, an alkyl group containing approximately 1 to approximately 10 carbon atom(s), an ether, SH, a thioether, or combinations thereof.

25. The electrochemical carbon monoxide sensor according to claim 14, wherein the carbonaceous material is selected from the group comprising graphene, graphite, amorphous carbon, carbon nanotubes, carbon fibers, or combinations thereof.

26. The electrochemical carbon monoxide sensor according to claim 14, further comprising a desiccant for retaining a liquid.

27. An electrochemical carbon monoxide sensor for use in a gas/fire detector, said electrochemical carbon monoxide sensor being exposed to a sample gas during normal sensing operation, comprising:

- a housing, wherein the housing comprises a sidewall, a top wall, and a bottom wall, and wherein the sidewall, the top wall and the bottom wall define a containment region for containing a micro electrode assembly therein, and further wherein the top wall of the housing comprises a gaseous diffusion aperture;

- wherein the micro electrode assembly comprises an anode, a cathode and an ion conducting membrane, and wherein the anode and the cathode are discrete elements, and wherein the ion conducting membrane permits ion transport between the anode and the cathode, and wherein the ion conducting membrane prevents electron conduction between the anode and the cathode;

- wherein the cathode comprises an oxygen reduction catalyst that comprises a pyrolysis product of a carbonaceous material and an organometallic coordination complex of a transition metal with a nitrogen containing macrocycle that has been deposited on the carbonaceous material; and

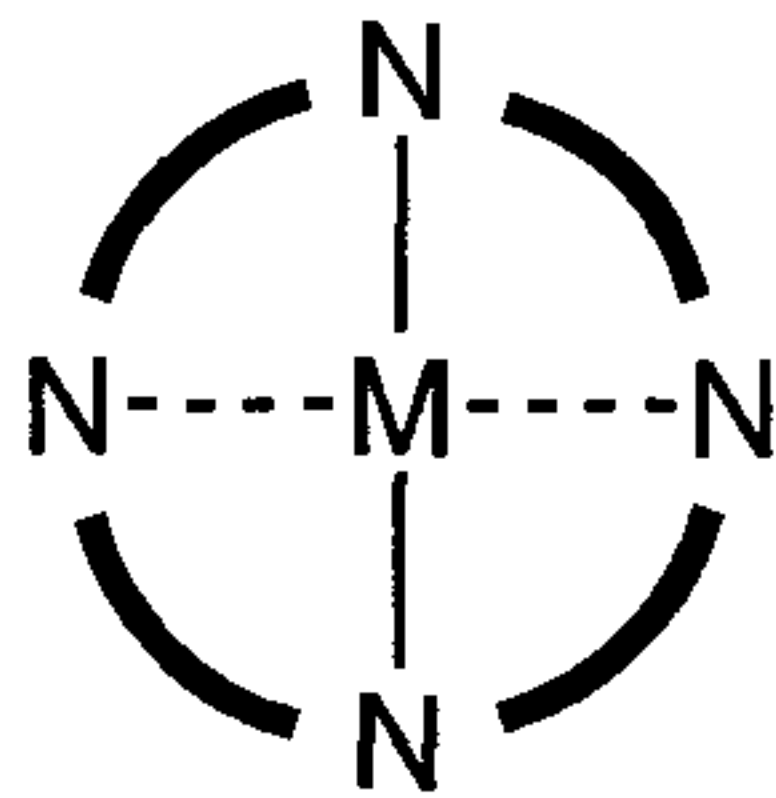
- wherein the anode and the cathode are configured to be exposed to the same sample gas during normal sensing operation.

28. The electrochemical carbon monoxide sensor according to claim 27, wherein the organometallic coordination complex comprises at least one of the group comprising substituted transition metal porphyrins, unsubstituted transition metal porphyrins, substituted transition metal tetrabenzoporphyrins, unsubstituted transition metal tetrabenzoporphyrins, substituted transition metal tetraphenylporphyrins, unsubstituted transition metal tetraphenylporphyrins, substituted transition metal tetraazaporphyrins, unsubstituted transition metal tetraazaporphyrins, substituted transition metal tetraazamacrocycles, unsubstituted transition metal tetraazamacrocycles, substituted transition metal phthalocyanines, unsubstituted transition metal phthalocyanines, substituted transition metal naphthalocyanines, unsubstituted transition metal naphthalocyanines, substituted transition metal bis(phthalocyanines), unsubstituted transition metal bis(phthalocyanines), substituted transition metal bis(naphthalocyanines), unsubstituted transition metal bis(naphthalocyanines), or combinations thereof.

29. The electrochemical carbon monoxide sensor according to claim 27, wherein the organometallic coordination complex comprises at least one of the group comprising substituted cobalt porphyrins, unsubstituted cobalt porphyrins, substituted cobalt tetrabenzoporphyrins, unsubstituted cobalt tetrabenzoporphyrins, substituted cobalt tetraphenylporphyrins, unsubstituted cobalt tetraphenylporphyrins, substituted cobalt tetraazaporphyrins, unsubstituted cobalt tetraazaporphyrins, substituted cobalt tetraazamacrocycles, unsubstituted cobalt tetraazamacrocycles, substituted cobalt metal phthalocyanines, unsubstituted cobalt phthalocyanines, substituted cobalt

naphthalocyanines, unsubstituted cobalt naphthalocyanines, substituted cobalt bis(phthalocyanines), unsubstituted cobalt bis(phthalocyanines), substituted cobalt bis(naphthalocyanines), unsubstituted cobalt bis(naphthalocyanines), or combinations thereof.

30. The electrochemical carbon monoxide sensor according to claim 27, wherein the organometallic coordination complex comprises a compound of formula (I):



(I)

- wherein N is a nitrogen atom and M comprises a transition metal ligated by a tetraazamacrocyclic.

31. An electrochemical carbon monoxide sensor for use in a gas/fire detector, said electrochemical carbon monoxide sensor being exposed to a sample gas during normal sensing operation, comprising:

- a housing having a containment region for containing a micro electrode assembly therein, and further wherein the housing comprises a gaseous diffusion aperture;

- wherein the micro electrode assembly comprises an anode, a cathode and an ion conducting membrane, and wherein the ion conducting membrane permits ion transport between the anode and the cathode, and wherein the ion conducting membrane prevents electron conduction between the anode and the cathode;

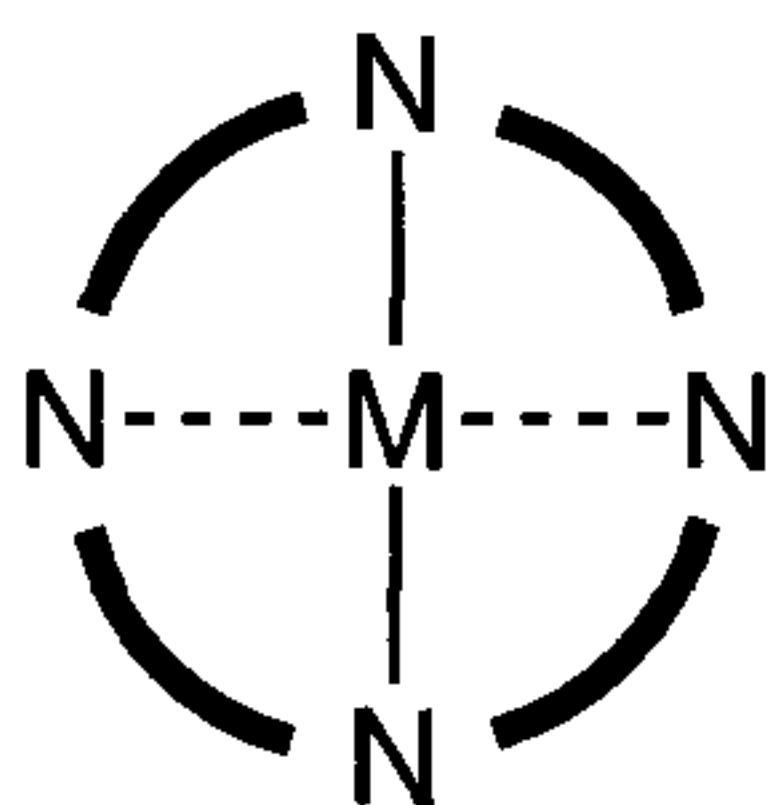
- wherein the cathode comprises an oxygen reduction catalyst that comprises a pyrolysis product of a carbonaceous material and an organometallic coordination complex of a transition metal with a nitrogen containing macrocycle that has been deposited on the carbonaceous material; and

- wherein the anode and the cathode are configured to be exposed to the same sample gas during normal sensing operation.

32. The electrochemical carbon monoxide sensor according to claim 31, wherein the organometallic coordination complex comprises at least one of the group comprising

substituted transition metal porphyrins, unsubstituted transition metal porphyrins, substituted transition metal tetrabenzoporphyrins, unsubstituted transition metal tetrabenzoporphyrins, substituted transition metal tetraphenylporphyrins, unsubstituted transition metal tetraphenylporphyrins, substituted transition metal tetraazaporphyrins, unsubstituted transition metal tetraazaporphyrins, substituted transition metal tetraazamacrocycles, unsubstituted transition metal tetraazamacrocycles, substituted transition metal phthalocyanines, unsubstituted transition metal phthalocyanines, substituted transition metal naphthalocyanines, unsubstituted transition metal naphthalocyanines, substituted transition metal bis(phthalocyanines), unsubstituted transition metal bis(phthalocyanines), substituted transition metal bis(naphthalocyanines), unsubstituted transition metal bis(naphthalocyanines), or combinations thereof.

33. The electrochemical carbon monoxide sensor according to claim 31, wherein the organometallic coordination complex comprises a compound of formula (I):



(I)

- wherein N is a nitrogen atom and M comprises a transition metal ligated by a tetraazamacrocycle.

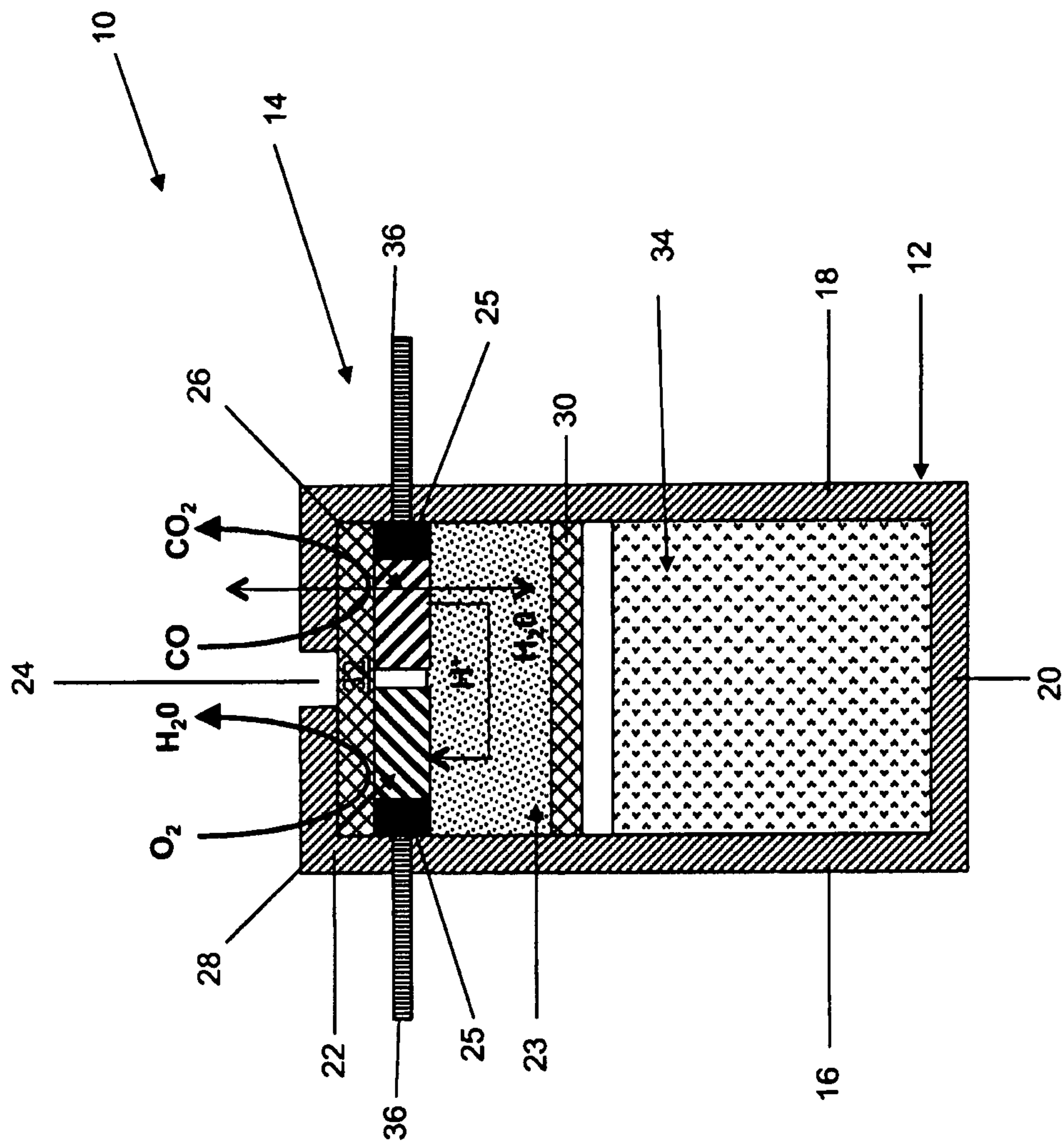


Figure 1A

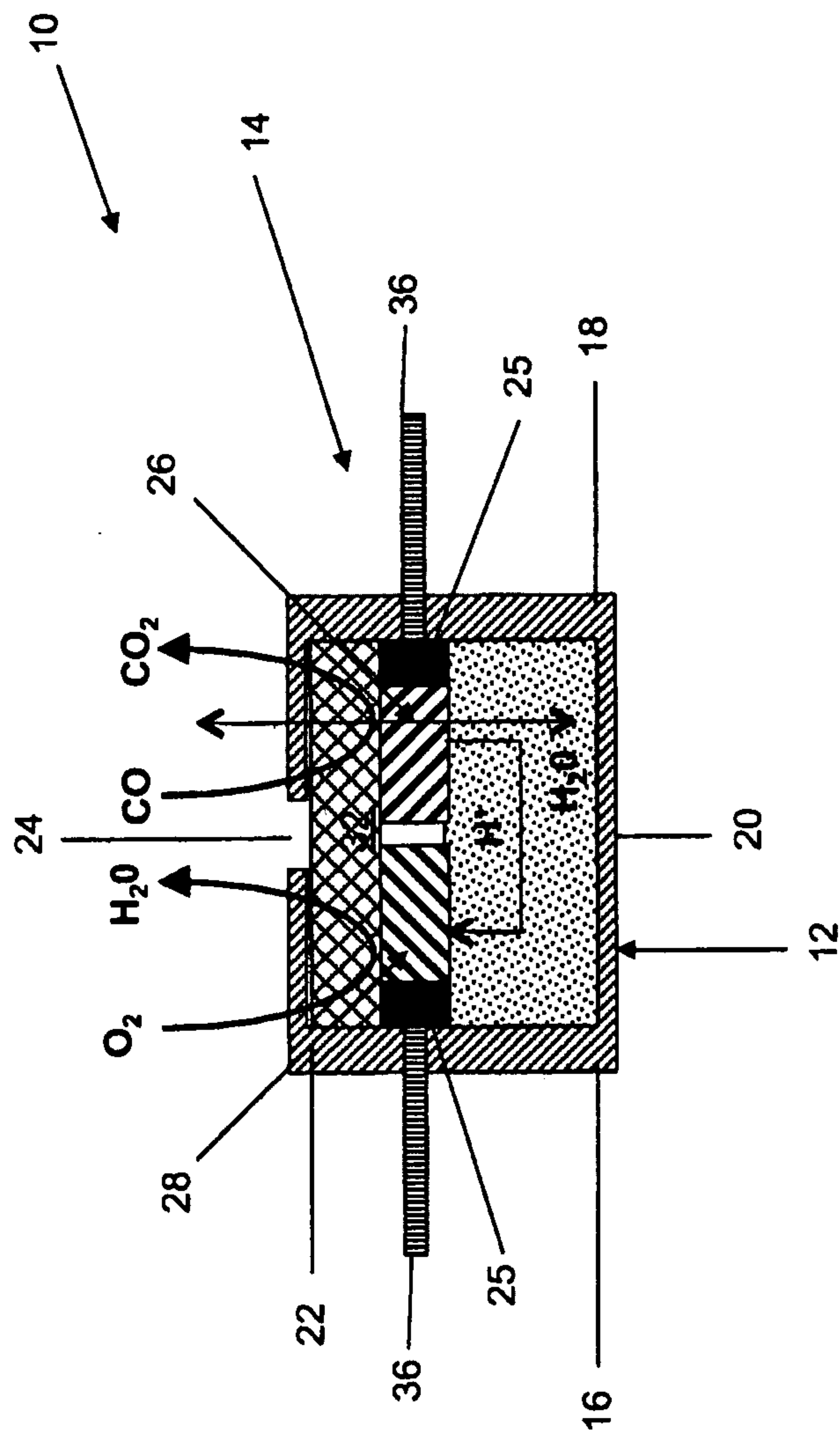


Figure 1B

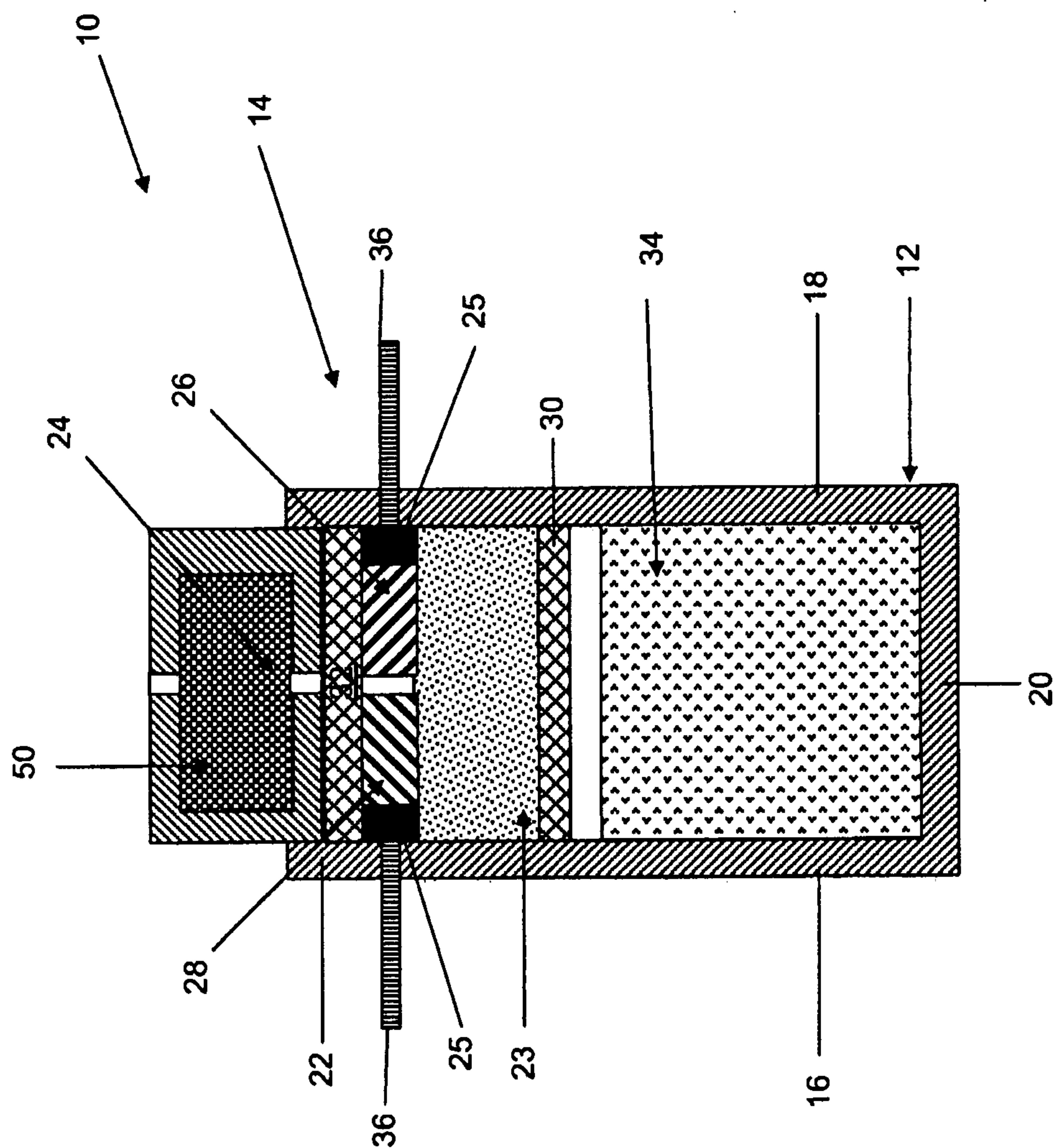


Figure 1C

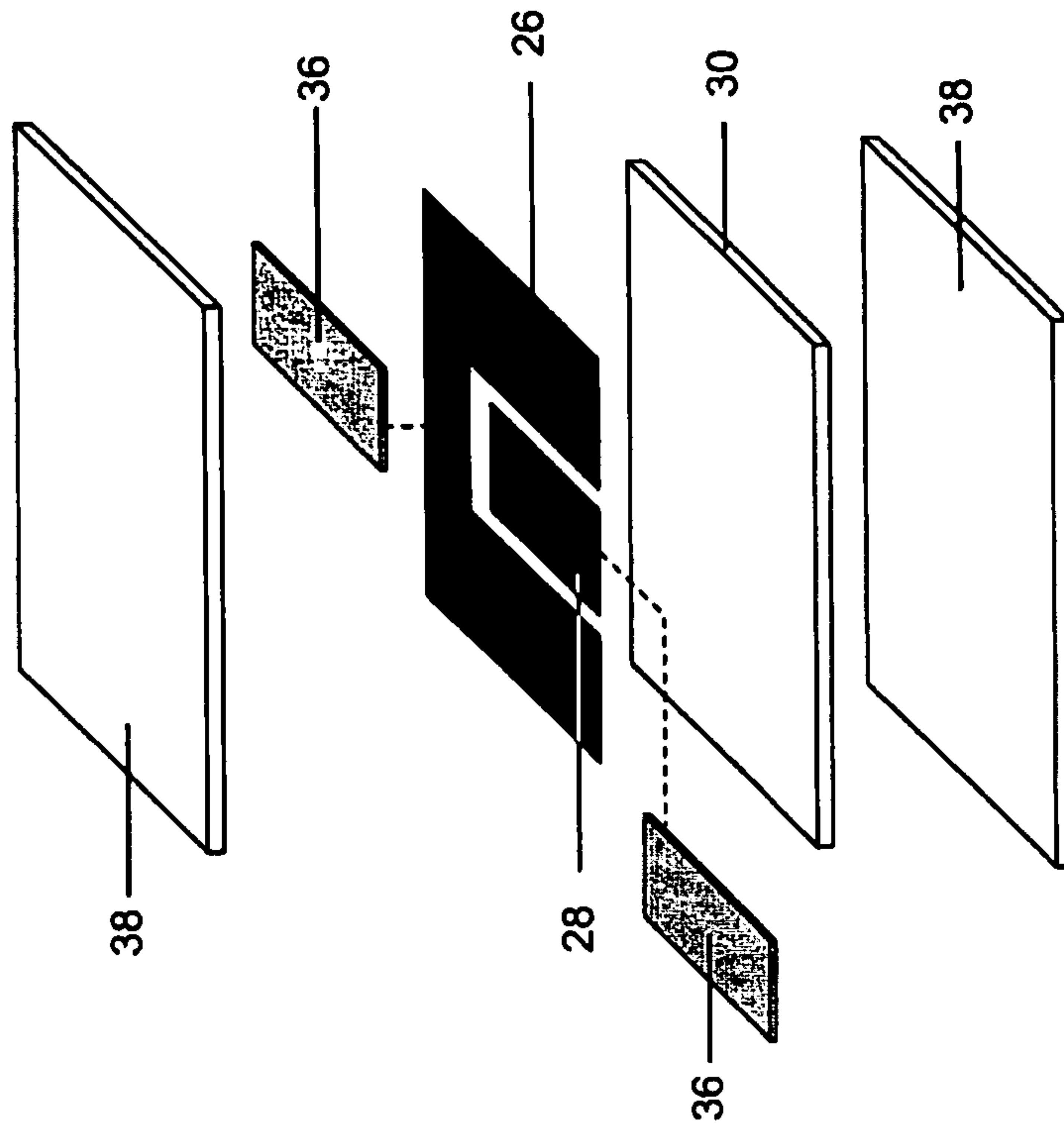


Figure 2B

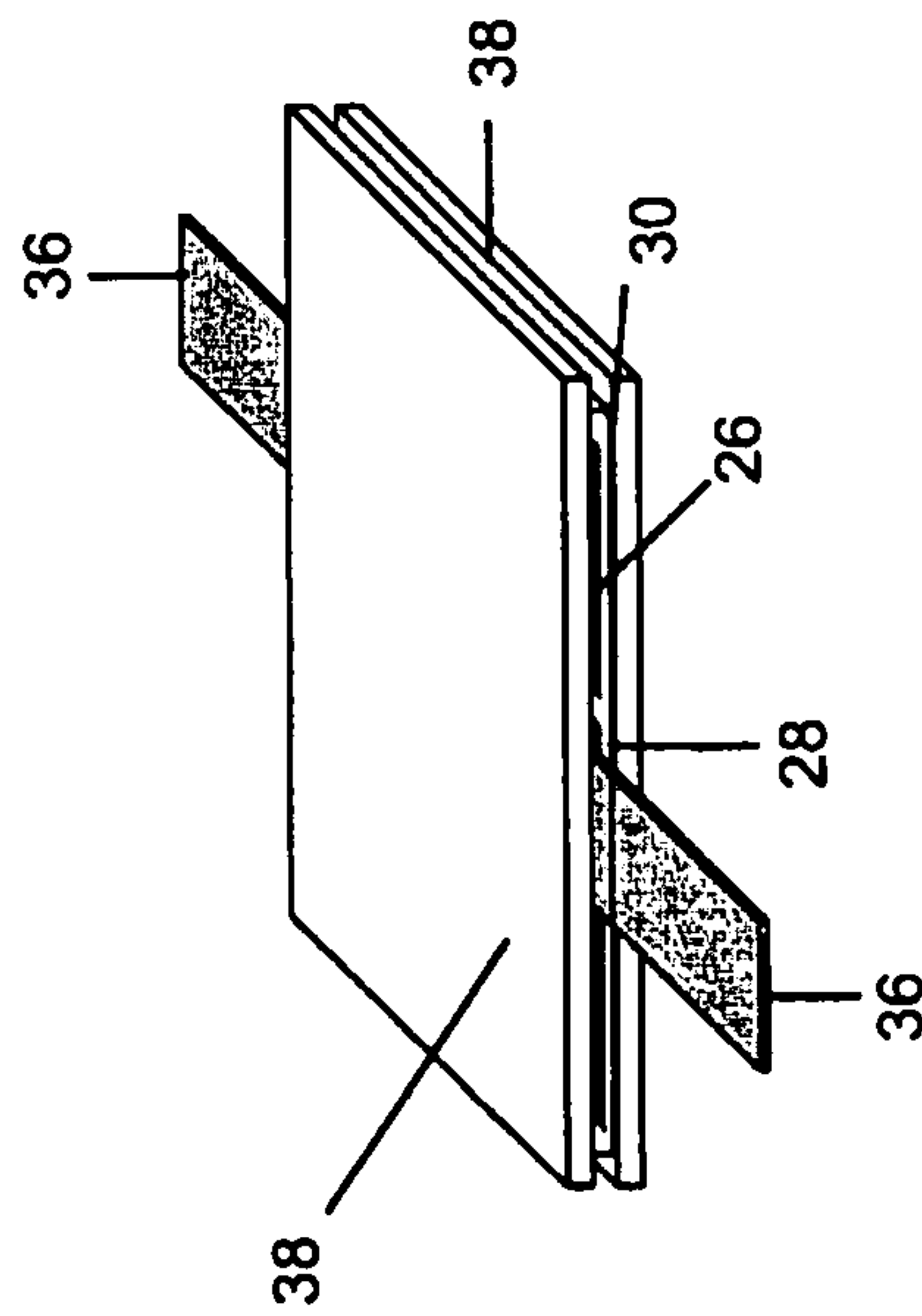


Figure 2A

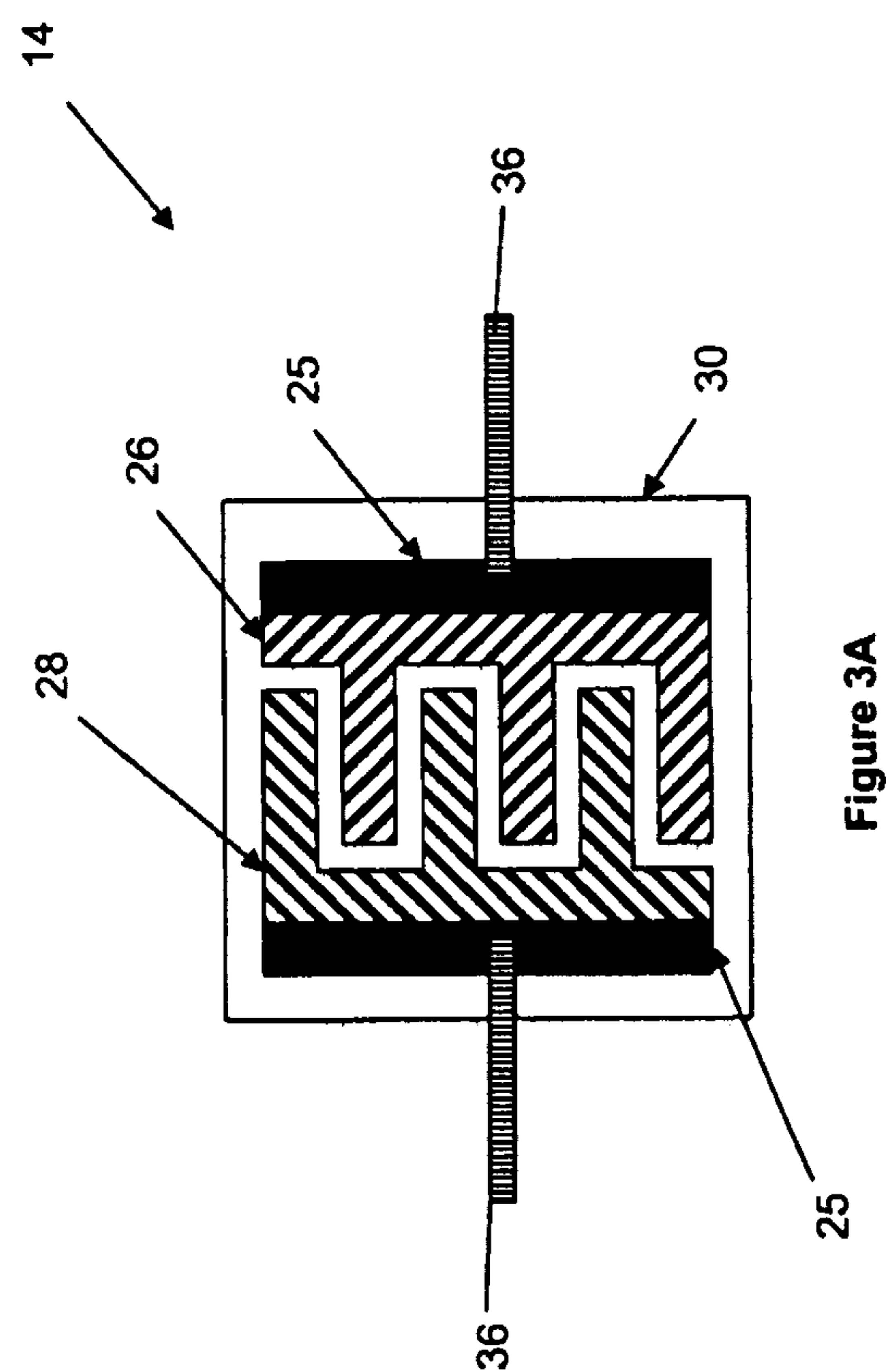


Figure 3A

Alternative Patterns

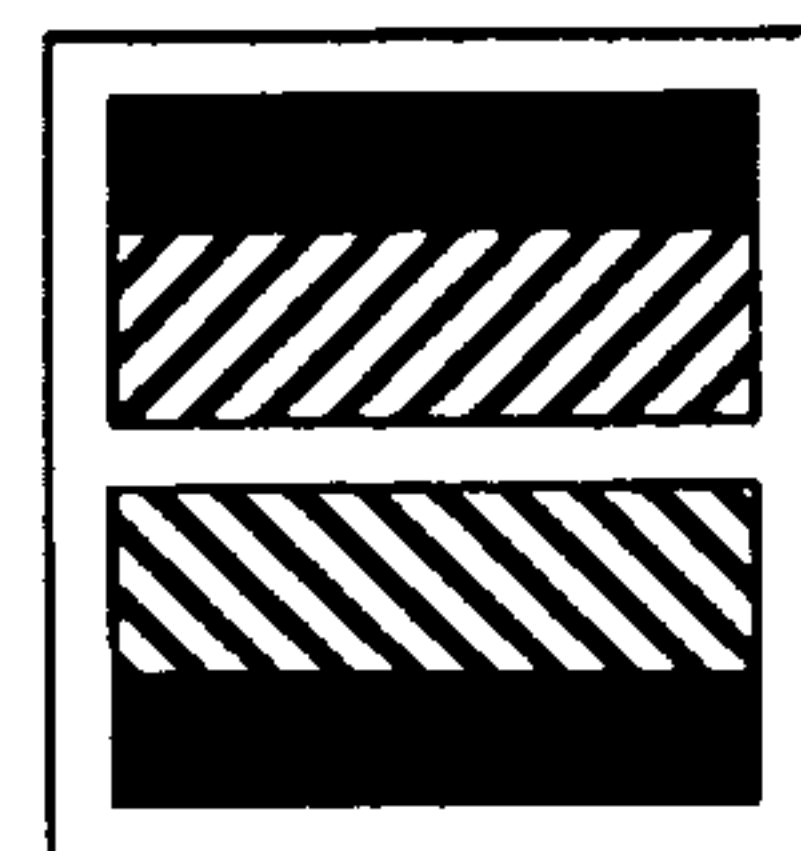


Figure 3B

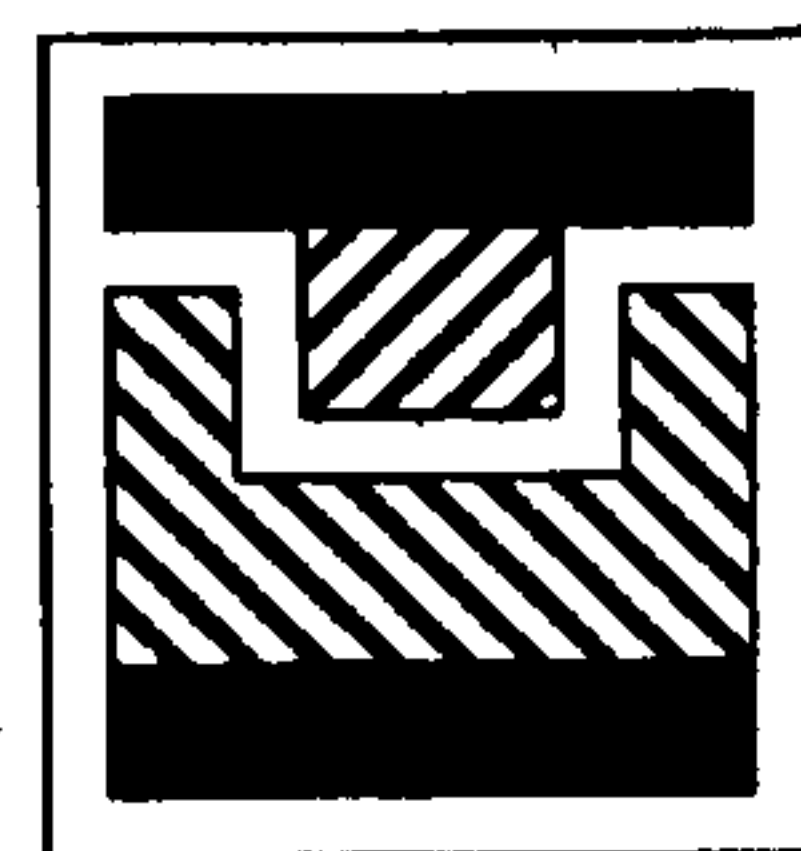


Figure 3C

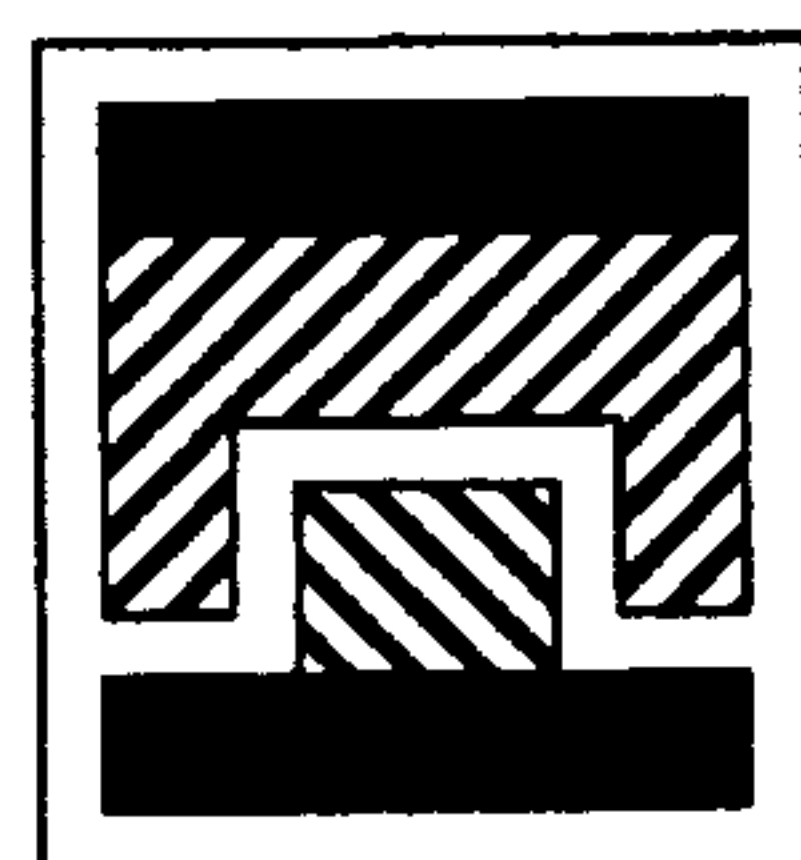
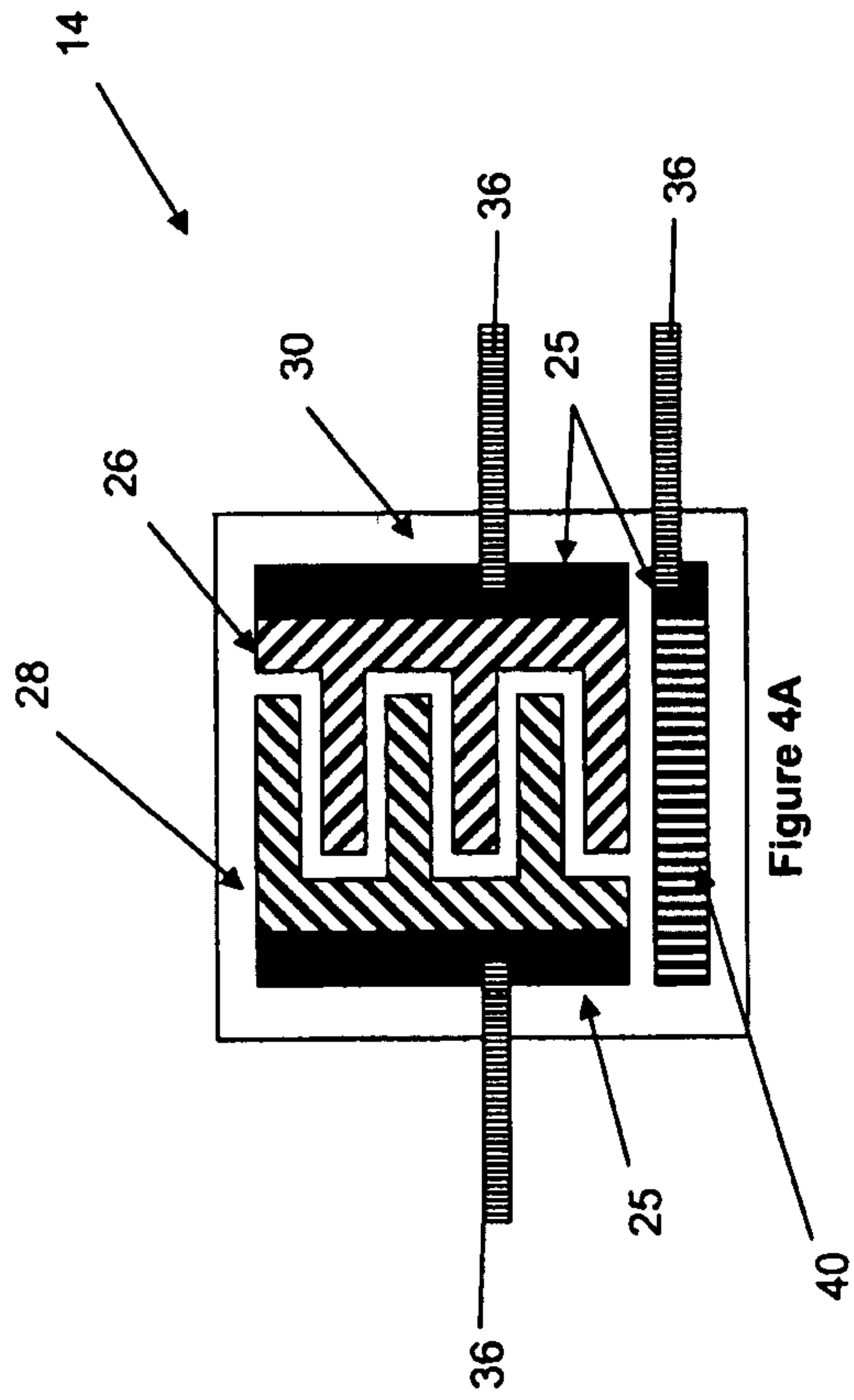
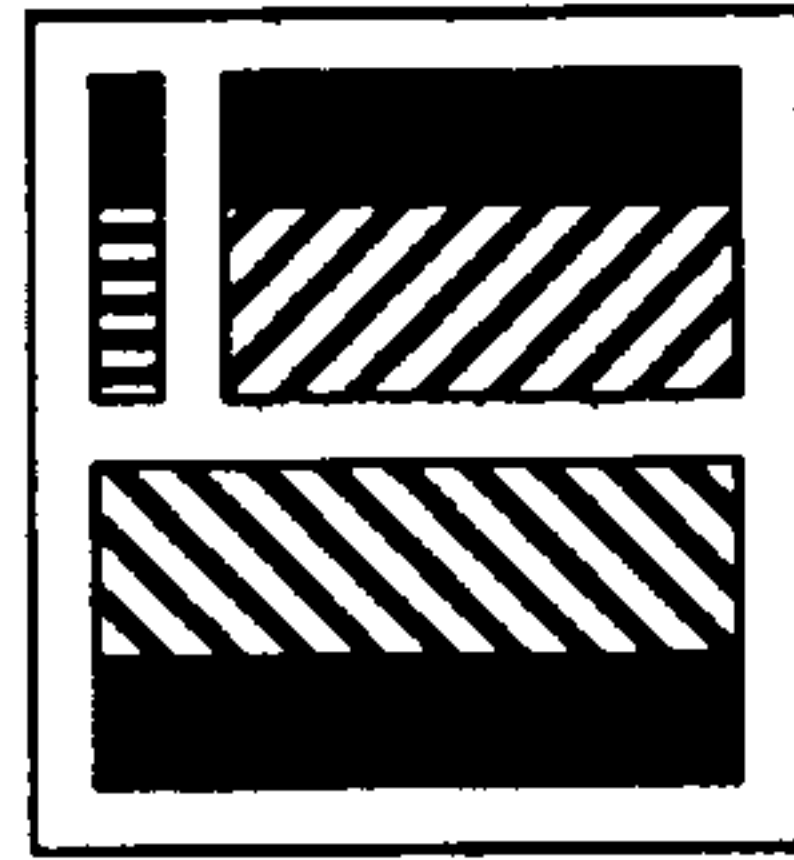
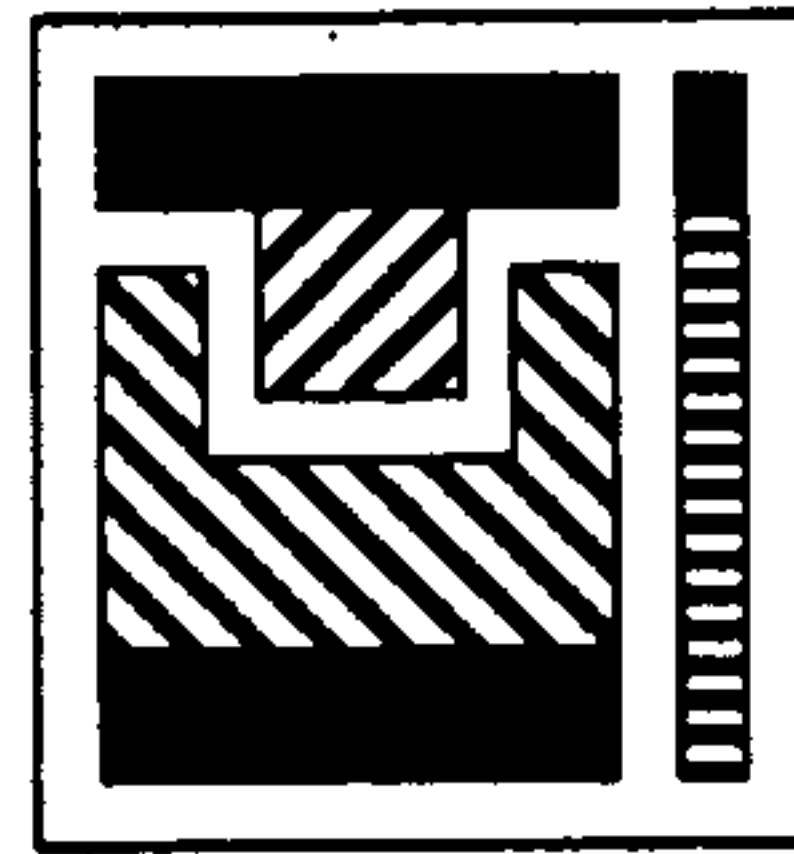
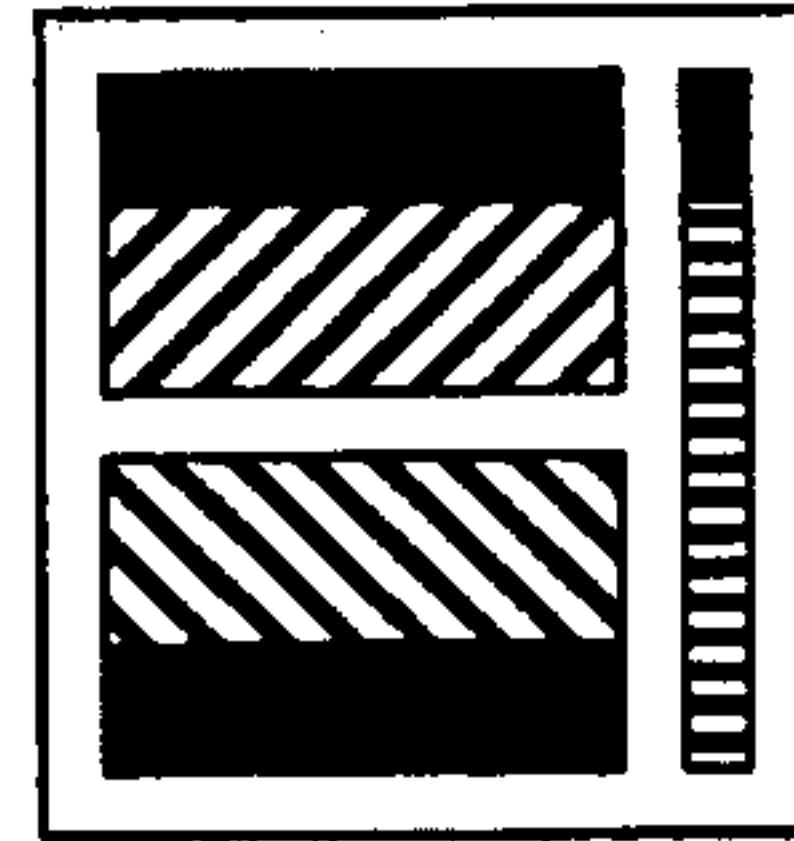


Figure 3D



Alternative Patterns



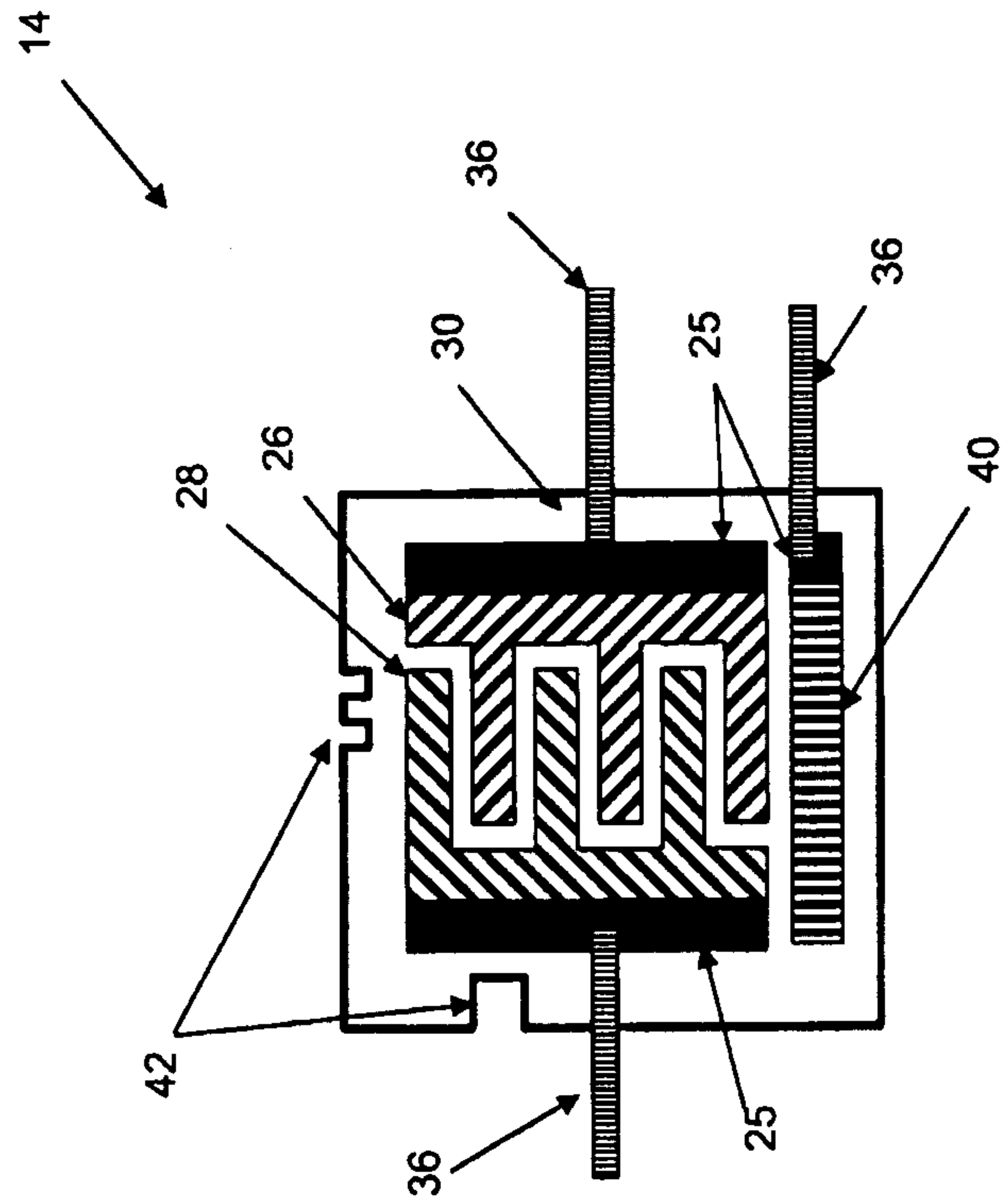


Figure 5

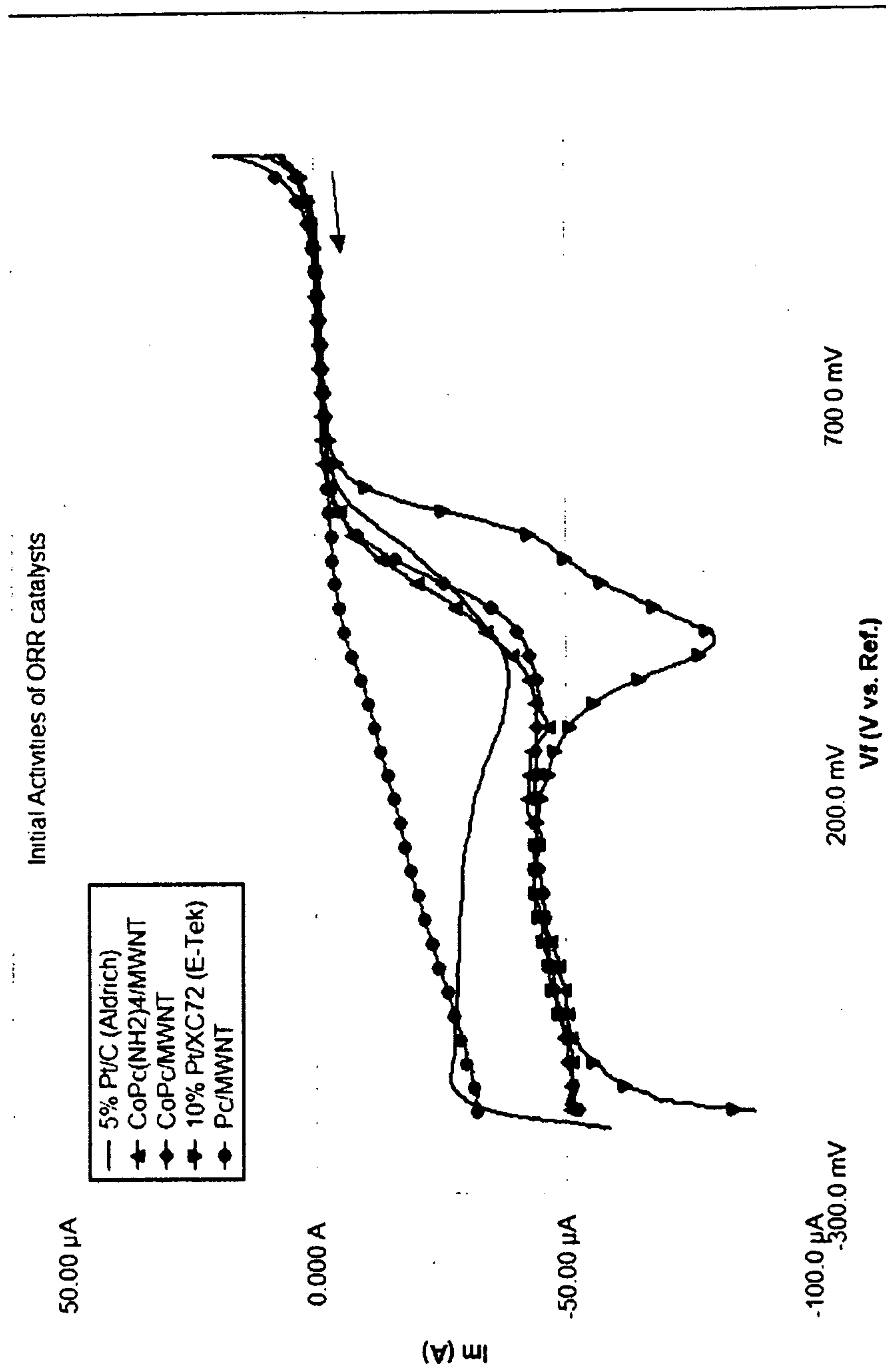


Figure 6

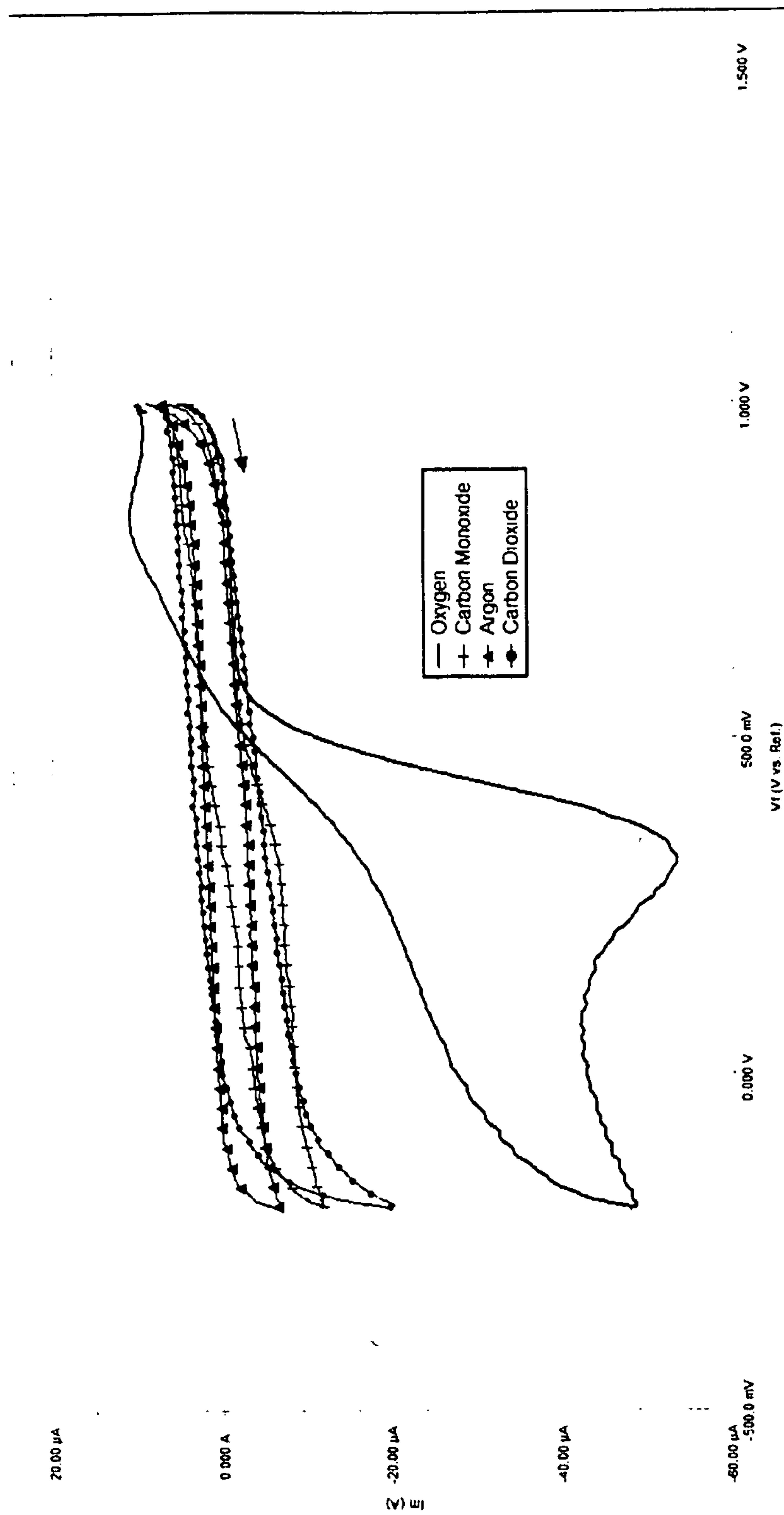


Figure 7

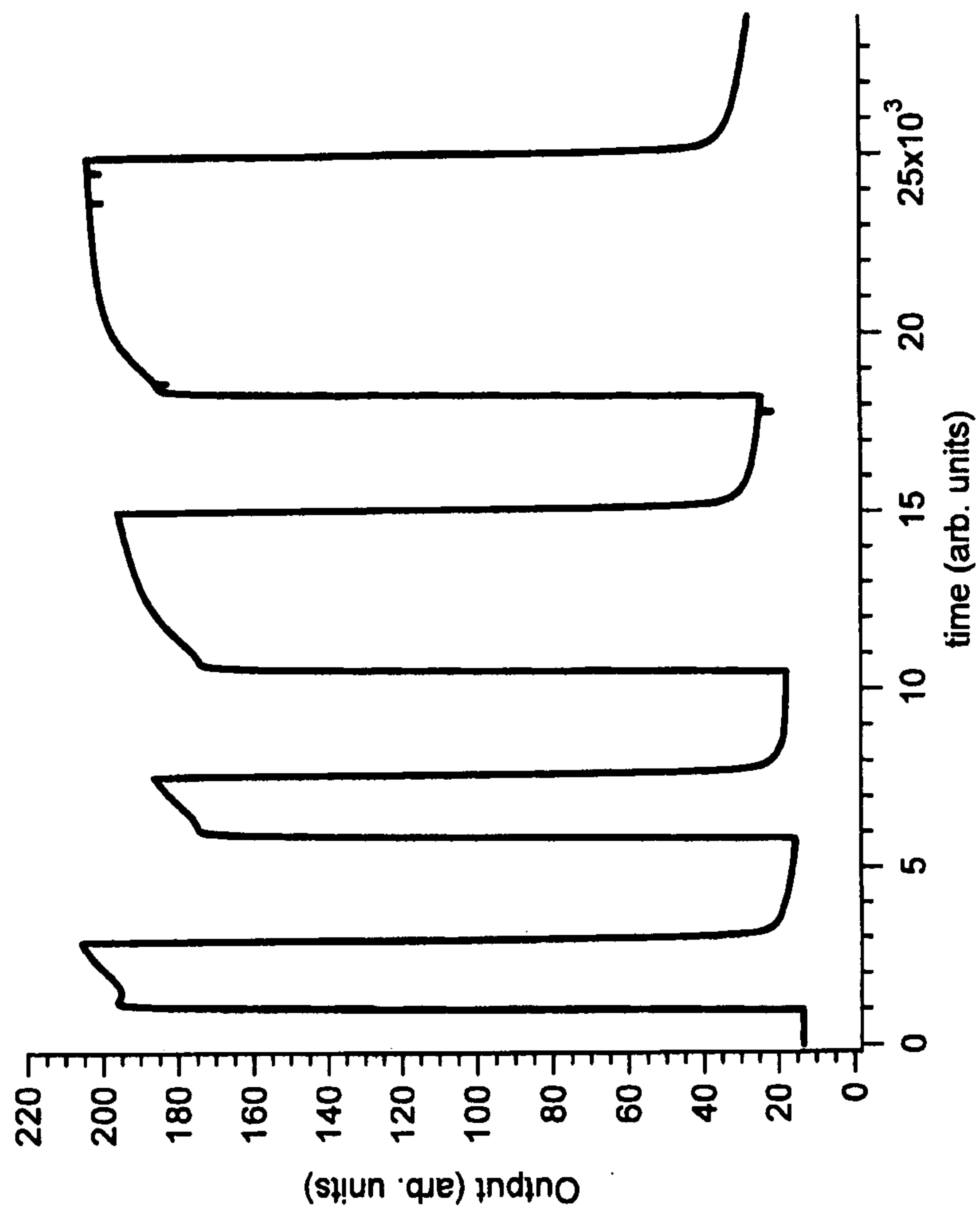


Figure 9a. Operation of Sensor 1 under 390 ± 10 ppm pulses of CO

Figure 8A

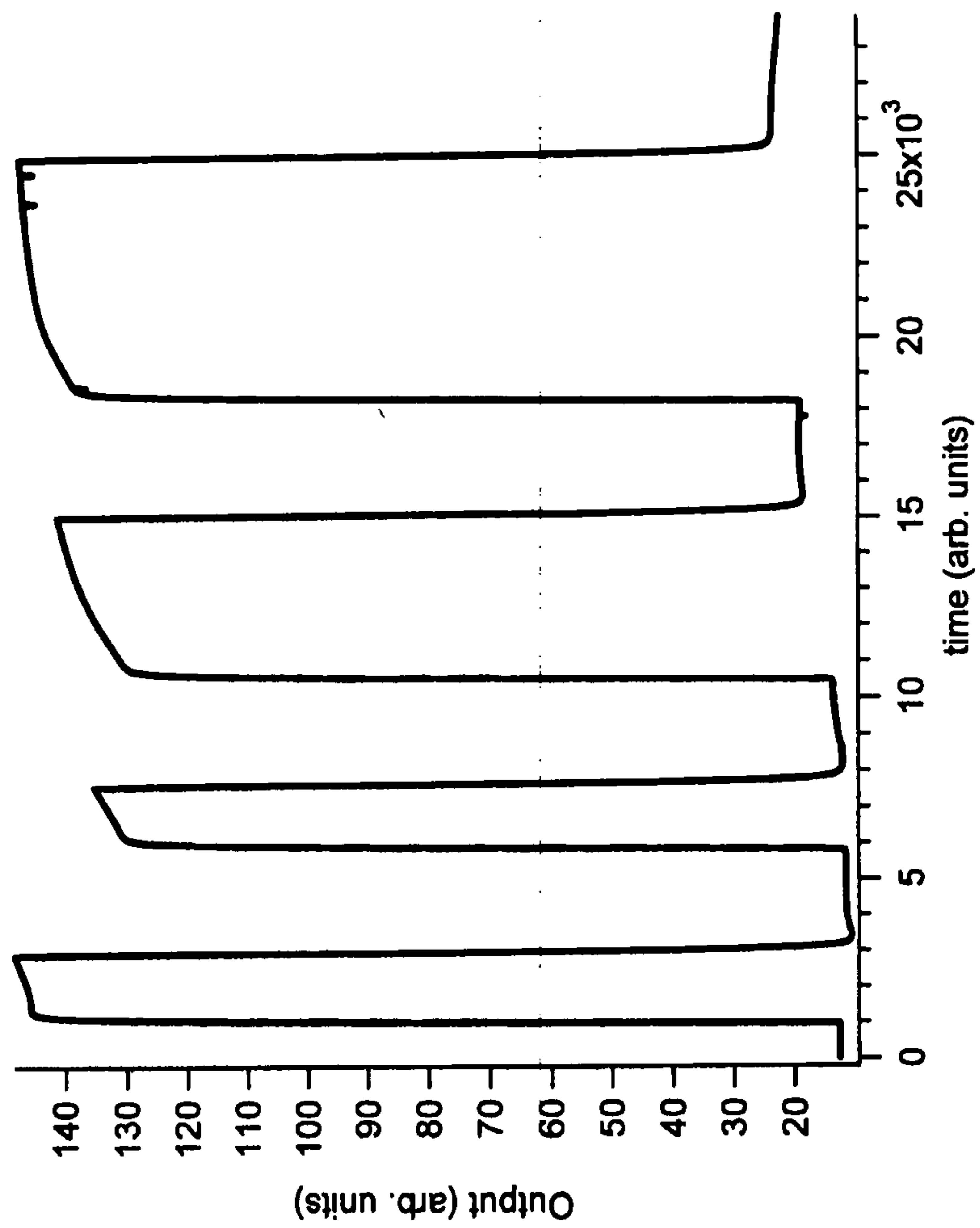
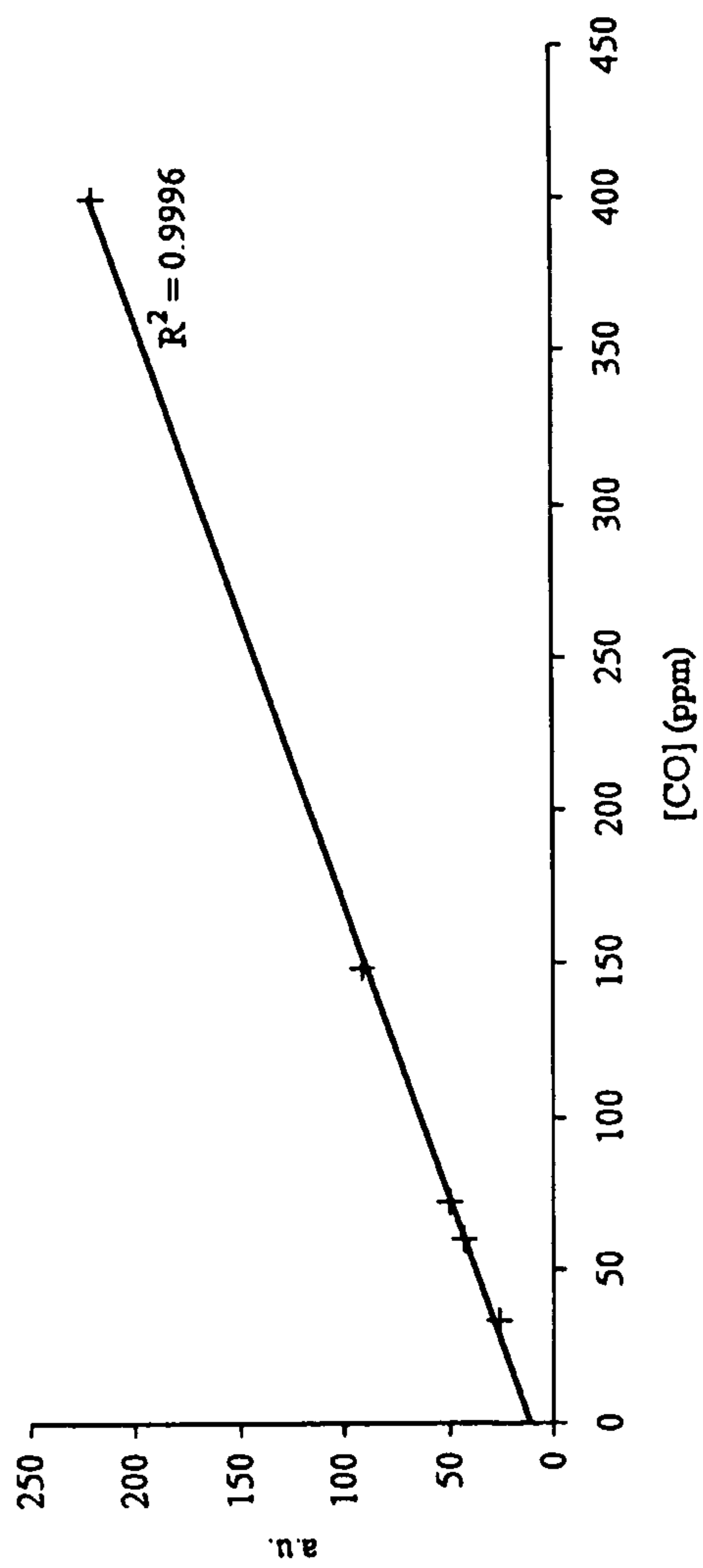


Figure 9b. Operation of Sensor 2 under 390±10 ppm pulses of CO

Figure 8B



Linear Response of CO Sensor from 30-400 ppm CO at 45% RH

Figure 9

