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(72) Inventeurs/Inventors:
NOHR, RONALD SINCLAIR, US;
MACDONALD, JOHN GAVIN, US

(73) Propriétaire/Owner:
KIMBERLY-CLARK WORLDWIDE, INC., US

(74) Agent: BORDEN LADNER GERVAIS LLP

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(54) Title: NEONANOPLASTS PRODUCED BY MICROEMULSION TECHNOLOGY AND INKS FOR INK JET PRINTING

(57) Abrégé/Abstract:
The present invention relates to colorant compositions containing neonanoplasts. The colorant compositions exhibit improved color brightness and brilliance due to the incorporation of one or more colorants in the neonanoplasts. The colorant compositions may be printed onto virtually any substrate. The colorant compositions of the present invention have particular utility in the area of printed textiles.

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(71) Applicant: KIMBERLY-CLARK WORLDWIDE, INC. [US/US]; 401 North Lake Street, Neenah, WI 54956 (US).

(72) Inventors: NOHR, Ronald, Sinclair; 8955 Nesbit Lakes Drive, Alpharetta, GA 30202 (US). MACDONALD, John, Gavin; 1472 Knollwood Terrace, Decatur, GA 30033 (US).

(74) Agents: WITHERS, James, D.; Jones & Askew, LLP, 2400 Monarch Tower, 3424 Peachtree Road, Atlanta, GA 30326 (US) et al.

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(54) Title: NEONANOPLASTS AND MICROEMULSION TECHNOLOGY FOR INKS AND INK JET PRINTING

(57) Abstract

The present invention relates to colorant compositions containing neonanoplasts. The colorant compositions exhibit improved color brightness and brilliance due to the incorporation of one or more colorants in the neonanoplasts. The colorant compositions may be printed onto virtually any substrate. The colorant compositions of the present invention have particular utility in the area of printed textiles.

NEONANOPLASTS PRODUCED BY MICROEMULSION TECHNOLOGY AND INKS FOR INK JET PRINTING

Technical Field

The present invention relates to colorant compositions containing neonanoplasts. The colorant compositions exhibit improved color brightness and brilliance due to the incorporation of one or more colorants in the neonanoplasts. The colorant compositions may be printed onto virtually any substrate. The colorant compositions of the present invention have particular utility in the area of printed textiles.

Background of the Invention

A major problem with colorants is that they tend to fade when exposed to electromagnetic radiation such as sunlight or artificial light and the like. It is believed that most of the fading of colorants when exposed to light is due to photodegradation mechanisms. These degradation mechanisms include oxidation or reduction of the colorants depending upon the environmental conditions in which the colorant is placed. Fading of a colorant also depends upon the substrate upon which they reside.

Product analysis of stable photoproducts and intermediates has revealed several important modes of photodecomposition. These include electron ejection from the colorant, reaction with ground-state or excited singlet state oxygen, cleavage of the central carbon-phenyl ring bonds to form amino substituted benzophenones, such as triphenylmethane dyes, reduction to form the colorless leuco dyes and electron or hydrogen atom abstraction to form radical intermediates.

Various factors such as temperature, humidity, gaseous reactants, including O_2, O_3, SO_2, and NO_2, and water soluble, nonvolatile photodegradation products have been shown to influence fading of colorants. The factors that effect colorant fading appear to exhibit a certain amount of interdependence. It is due to this complex behavior that observations for the fading of a particular colorant on a particular substrate cannot be applied to colorants and substrates in general.

Under conditions of constant temperature it has been observed that an increase in the relative humidity of the atmosphere increases the fading of a colorant for a variety of colorant-substrate systems (e.g., McLaren, K., *J. Soc. Dyers Colour*, 1956, 72, 527). For example, as the relative humidity of the atmosphere increases, a fiber may swell because the moisture content of the fiber increases. This aids diffusion of gaseous reactants through the substrate structure.

The ability of a light source to cause photochemical change in a colorant is also dependent upon the spectral distribution of the light source, in particular the proportion of radiation of wavelengths most effective in causing a change in the colorant and the quantum yield of colorant degradation as a function of wavelength. On the basis of photochemical principles, it would be expected that light of higher energy (short wavelengths) would be more effective at causing fading than light of lower energy (long wavelengths). Studies have revealed that this is not always the case. Over 100 colorants of different classes were studied and found that generally the most unstable were faded more efficiently by visible light while those of higher lightfastness were degraded mainly by ultraviolet light (McLaren, K., J. *Soc. Dyers Colour*, 1956, 72, 86).

The influence of a substrate on colorant stability can be extremely important. Colorant fading may be retarded or promoted by a chemical group within the substrate. Such a group can be a ground-state species or an excited-state species. The porosity of the substrate is also an important factor in colorant stability. A high porosity can promote fading of a colorant by facilitating penetration of moisture and gaseous reactants into the substrate. A substrate may also act as a protective agent by screening the colorant from light of wavelengths capable of causing degradation.

The purity of the substrate is also an important consideration whenever the photochemistry of dyed technical polymers is considered. For example, technical-grade cotton, viscose rayon, polyethylene, polypropylene, and polyisoprene are known to contain carbonyl group impurities. These impurities absorb light of wavelengths greater than 300 nm, which are present in sunlight, and so, excitation of these impurities may lead to reactive species capable of causing colorant fading (van Beek, H.C.A., *Col. Res. Appl.*, 1983, 8(3), 176).

Mother nature protects naturally-occurring colorants from one or more of the above-described photodegradation mechanisms by surrounding the naturally-occurring colorants with a cell wall. The cell wall prevents destructive materials, such as O_2 gas, from reaching the colorant. The result is a colorant which maintains its brilliance, brightness and beauty even when exposed to sunlight day after day.

What is needed in the art is a colorant system which provides protection to a colorant in much the same way that nature protects colorants. There exists a need for methods and compositions which are capable of stabilizing a wide variety of colorants, regardless of the stability of the colorant, from the effects of both sunlight and artificial light.

Summary of the Invention

The present invention addresses the needs described above by providing compositions and methods for stabilizing colorants against radiation including radiation in the visible wavelength range. The present invention provides a system for shielding a colorant from destructive forces, such as oxidants and reductants. By providing a protective shield for the colorant, very unstable colorful dyes may be used in a wide variety of printing applications which were believed to be impossible applications due to rapid degradation of the dye.

The present invention is directed to neonanoplasts formed by microemulsion technology. The neonanoplasts contain one or more colorants and optionally colorant stabilizers. The neonanoplasts comprise a polymeric membrane which prevents degradable materials from reaching the colorant. The neonanoplasts may be incorporated into a variety of liquid mediums to form colorant compositions.

The present invention is further directed to a method of stabilizing a colorant by encapsulating the colorant in a polymeric membrane, forming a neonanoplast. In one embodiment of the present invention, one or more colorant stabilizers are also encapsulated in the polymeric membrane, creating multiple levels of colorant protection from photodegradable mechanisms.

The present invention is also directed to colorant compositions containing the above-described neonanoplasts. The colorant compositions may be applied to any substrate to impart a color to the substrate. In one embodiment of the present invention, a colorant composition comprising neonanoplasts, a liquid medium and a pre-polymer is coated onto a substrate and subsequently exposed to radiation to fix the neonanoplast to the substrate via the polymerization of the pre-polymer.

In another embodiment of the present invention, neonanoplasts are present in a polymer coating of a heat transfer product, such as is used for transferring graphic images onto clothing.

The neonanoplasts are particularly effective in ink jet inks. Use of the neonanoplasts, as described herein, intensifies the colors and stabilizes the colorants when exposed to light and other potentially degrading conditions. Additionally, the neonanoplasts are particularly effective in coatings for paper products and textiles.

These and other features and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed embodiments and the appended claims.

Detailed Description of the Invention

The present invention is directed to neonanoplasts formed by microemulsion technology. Neonanoplasts are spherically-shaped polymeric membranes which encapsulates a colorant, and optionally other materials, to prevent degradable materials from reaching the colorant. Neonanoplasts can be formed by a microemulsion process. Neonanoplasts may have an average particle size of less than about 1000 nanometers (nm), desirably less than 500 nm. The neonanoplasts may be incorporated into a variety of mediums to form colorant compositions.

The present invention is further directed to a method of stabilizing a colorant by encapsulating the colorant in a polymeric membrane, forming a neonanoplast. In one embodiment of the present invention, one or more colorant stabilizers are encapsulated in the polymeric membrane, creating multiple levels of colorant protection from photodegradable mechanisms. Suitable colorant stabilizers include any colorant stabilizer which does not negatively effect the polymeric membrane of the neonanoplast.

In order to describe the various embodiments of the present invention, the following definitions are provided. As used herein, the term "microemulsion" is used herein to mean a multiple phase system containing, at the minimum, an aqueous phase and a non-aqueous phase in physical contact with one another.

As used herein, the term "colorant" is meant to include, without limitation, any material which typically will be an organic material, such as an organic colorant or dye. The term is meant to include a single material or a mixture of two or more materials.

The term "light-stable" is used herein to mean that the colorant, when encapsulated within a neonanoplast and/or associated with a colorant stabilizing molecules, is more stable to electromagnetic radiation, including, but not limited to, sunlight or artificial light, than when the colorant is not encapsulated by a neonanoplast and/or associated with such a compound.

The term "molecular includant," as used herein, is intended to mean any substance having a chemical structure which defines at least one cavity. That is, the molecular includant is a cavity-containing structure. As used herein, the term "cavity" is meant to include any opening or space of a size sufficient to accept at least a portion of the colorant.

The term "functionalized molecular includant" is used herein to mean a molecular includant to which one or more molecules of a colorant stabilizer are covalently coupled to each molecule of the molecular includant. The term "degree of substitution" is used herein to refer to the number of these molecules or leaving groups (defined below) which are covalently coupled to each molecule of the molecular includant.

The term "derivatized molecular includant" is used herein to mean a molecular includant having more than two leaving groups covalently coupled to each molecule of molecular includant. The

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term "leaving group" is used herein to mean any leaving group capable of participating in a bimolecular nucleophilic substitution reaction. Examples of molecular includants include, but are not limited to, the cyclodextrins.

The term "artificial light" is used herein to mean light having a relatively broad bandwidth that is produced from conventional light sources, including, but not limited to, conventional incandescent light bulbs and fluorescent light bulbs.

Forming Neonanoplasts

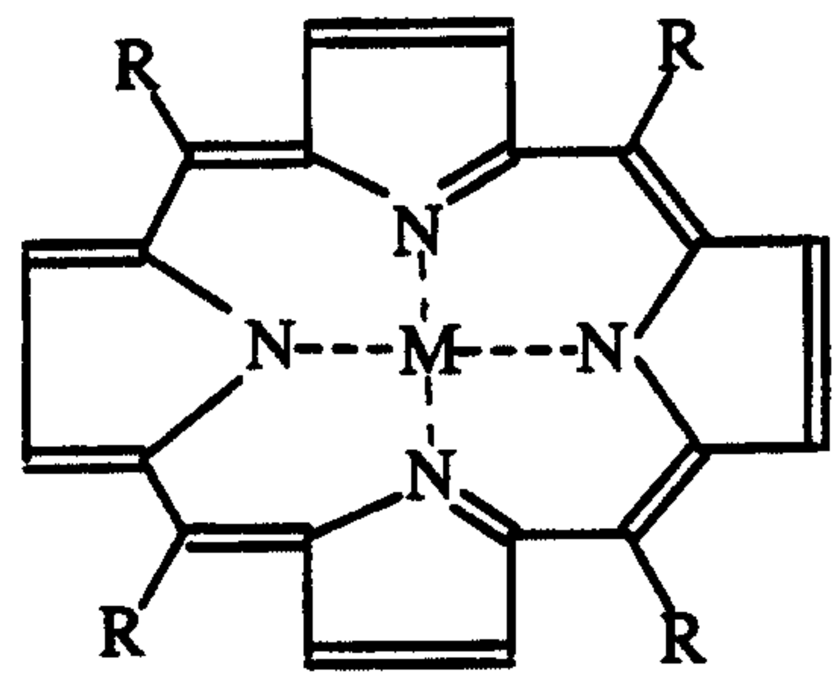
The present invention is further directed to a method of forming neonanoplasts. One method of forming the neonanoplasts of the present invention comprises forming a non-aqueous solution containing an organic solvent and a surfactant. Suitable organic solvents include, but are not limited to, *n*-hexane, heptane, octane, *n*-alkanes, branched alkanes. Suitable surfactants include, but are not limited to, Aerosol OT or dioctyl sodium sulfosuccinate, TRITON® X-100 and fatty acid salts. In a separate container, an aqueous solution is prepared containing at least one monomer and at least one colorant. Suitable monomers include, but are not limited to, acrylates, acrylamides and methacrylates.

Suitable colorants include, but are not limited to, dyes and pigments. The colorant may be an organic dye. Organic dye classes include, by way of illustration only, triarylmethyl dyes, such as Malachite Green Carbinol base {4-(dimethylamino)-a-[4-(dimethylamino)phenyl]-a-phenyl-benzene-methanol}, Malachite Green Carbinol hydrochloride {N-4-[[4-(dimethylamino)phenyl]phenyl-methylene]-2,5-cyclohexyldien-1-ylidene]-N-methyl-methanaminium chloride or bis[*p*-(dimethylamino)phenyl]phenylmethylium chloride}, and Malachite Green oxalate {N-4-[[4-(dimethylamino)-phenyl]-phenylmethylene]-2,5-cyclohexyldien-1-ylidene]-N-methyl-methanaminium chloride or bis[*p*-(dimethylamino)-phenyl]phenylmethylium oxalate}; monoazo dyes, such as Cyanine Black, Chrysoidine [Basic Orange 2; 4-(phenylazo)-1,3-benzenediamine monohydrochloride], Victoria Pure Blue BO, Victoria Pure Blue B, basic fuschin and ß-Naphthol Orange; thiazine dyes, such as Methylene Green, zinc chloride double salt [3,7-bis(dimethylamino)-6-nitrophenothiazin-5-ium chloride, zinc chloride double salt]; oxazine dyes, such as

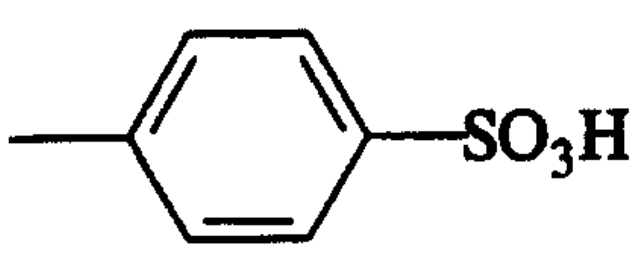
Lumichrome (7,8-dimethylalloxazine); naphthalimide dyes, such as Lucifer Yellow CH {6-amino-2-[(hydrazino-carbonyl)amino]-2,3-dihydro-1,3-dioxo-1H-benz[de]iso-quinoline-5,8-disulfonic acid dilithium salt}; azine dyes, such as Janus Green B {3-(diethylamino)-7-[[4-(dimethyl-amino)phenyl]azo]-5-phenylphenazinium chloride}; cyanine dyes, such as Indocyanine Green {Cardio-Green or Fox Green; 2-[7-[1,3-dihydro-1,1-dimethyl-3-(4-sulfobutyl)-2H-benz[e]indol-2-ylidene]-1,3,5-heptatrienyl]-1,1-dimethyl-3-(4-sulfobutyl)-1H-benz[e]indolium hydroxide inner salt sodium salt}; indigo dyes, such as Indigo {Indigo Blue or Vat Blue 1; 2-(1,3-dihydro-3-oxo-2H-indol-2-ylidene)-1,2-dihydro-3H-indol-3-one}; coumarin dyes, such as 7-hydroxy-4-methyl-coumarin (4-methylumbelliferone); benzimidazole dyes, such as Hoechst 33258 [bisbenzimide or 2-(4-hydroxyphenyl)-5-(4-methyl-1-piperazinyl)-2,5-bi-1H-benzimidazole trihydro-chloride pentahydrate]; paraquinoidal dyes, such as Hematoxylin {Natural Black 1; 7,11b-dihydrobenz[b]-indeno[1,2-d]pyran-3,4,6a,9,10(6H)-pentol}; fluorescein dyes, such as Fluoresceinamine (5-aminofluorescein); diazonium salt dyes, such as Diazo Red RC (Azoic Diazo No. 10 or Fast Red RC salt; 2-methoxy-5-chlorobenzenediazonium chloride, zinc chloride double salt); azoic diazo dyes, such as Fast Blue BB salt (Azoic Diazo No. 20; 4-benzoylamino-2,5-diethoxy-benzene diazonium chloride, zinc chloride double salt); phenylenediamine dyes, such as Disperse Yellow 9 [N-(2,4-dinitrophenyl)-1,4-phenylenediamine or Solvent Orange 53]; diazo dyes, such as Disperse Orange 13 [Solvent Orange 52; 1-phenylazo-4-(4-hydroxyphenylazo)naphthalene]; anthra-quinone dyes, such as Disperse Blue 3 [Celliton Fast Blue FFR; 1-methylamino-4-(2-hydroxyethylamino)-9,10-anthraquinone], Disperse Blue 14 [Celliton Fast Blue B; 1,4-bis(methylamino)-9,10-anthraquinone], and Alizarin Blue Black B (Mordant Black 13); trisazo dyes, such as Direct Blue 71 {Benzo Light Blue FFL or Sirius Light Blue BRR; 3-[(4-[(4-[(6-amino-1-hydroxy-3-sulfo-2-naphthalenyl)azo]-6-sulfo-1-naphthalenyl)-azo]-1-naphthalenyl)azo]-1,5-naphthalenedisulfonic acid tetrasodium salt}; xanthene dyes, such as 2,7-dichloro-fluorescein; proflavine dyes, such as 3,6-diaminoacridine hemisulfate (Proflavine); sulfonaphthalein dyes, such as Cresol Red (o-cresolsulfonaphthalein); phthalocyanine dyes, such as Copper Phthalocyanine {Pigment Blue 15; (SP-4-1)-[29H,31Hphthalocyanato(2-)-N^{29},N^{30},N^{31},N^{32}]copper}; carotenoid dyes, such as trans-ß-carotene (Food Orange 5); carminic acid dyes, such as Carmine, the aluminum or calcium-aluminum lake of carminic acid (7-a-D-glucopyranosyl-9,10-dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxo-2-anthracene-carbonylic acid); azure dyes, such as Azure A [3-amino-7-(dimethylamino)phenothiazin-5-ium chloride or 7-(dimethyl-amino)-3-imino-3H-phenothiazine hydrochloride]; and acridine dyes, such as Acridine Orange [Basic Orange 14; 3,8-bis(dimethylamino)acridine hydrochloride, zinc chloride double salt] and Acriflavine (Acriflavine neutral; 3,6-diamino-10-methylacridinium chloride mixture with 3,6-acridine-diamine).

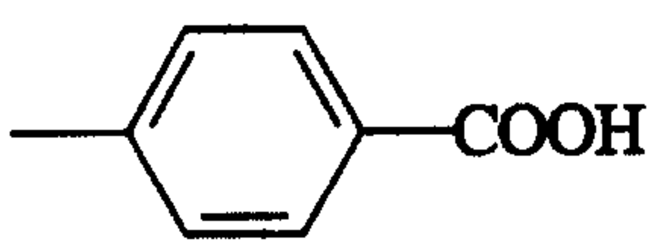
The aqueous solution is added to the non-aqueous solution while stirring to form a mixture. To the mixture is added an initiator to polymerize the one or more monomers of the aqueous phase. As the polymerization reaction proceeds, the colorant of the aqueous phase is encapsulated by the polymerizing monomer to form microemulsion spheres within the non-aqueous phase. The non-aqueous phase is removed to yield an aqueous phase containing the neonanoplasts. In order to remove the surfactant from the aqueous phase, dialysis bags or some other separation means are used to separate the surfactant from the aqueous phase containing the neonanoplasts. Water is then removed to yield neonanoplasts. The resulting neonanoplasts may have an average particle size of less than about 1000 nm. Desirably, the neonanoplasts have an average particle size of less than about 500 nm. More desirably, the neonanoplasts have an average particle size of less than about 100 nm.

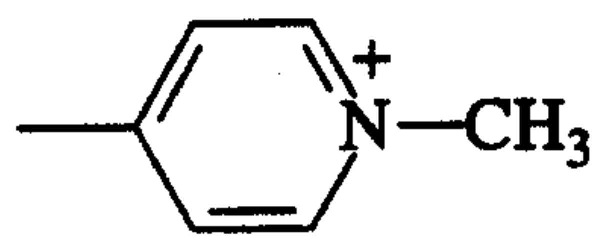
In one embodiment of the present invention, one or more colorant stabilizers are associated with the colorant. By incorporating one or more colorant stabilizers into the aqueous solution described above, colorant stabilizers may be encapsulated within the neonanoplasts along with the colorant. Suitable colorant stabilizers for use in the present invention include, but are not limited to, colorant stabilizers disclosed in U.S. Patents Nos. 6,099,628; 5,782,963; 5,855,655; and 5,891,229; all of which are assigned to Kimberly-Clark Worldwide, Inc. In a further embodiment of the present invention, suitable colorant stabilizers include, but are not limited to, a porphine, a metal, a metal salt, a molecular includant or a combination thereof. Particularly suitable porphines include, but are not limited to, porphines having the following structure:



wherein R is any proton-donating moiety and M is iron, cobalt or copper. Desirably, R is SO3H,

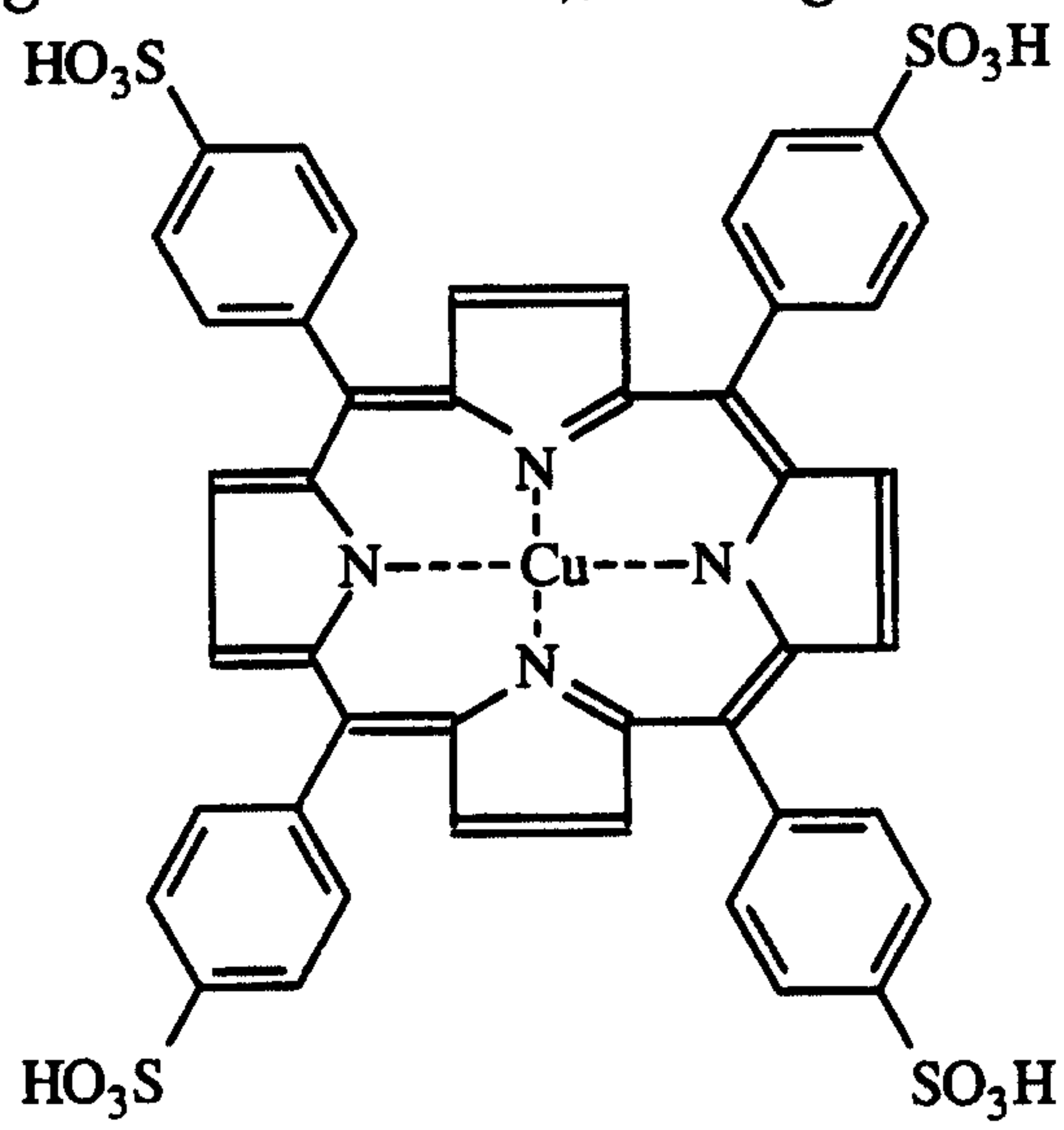


, 

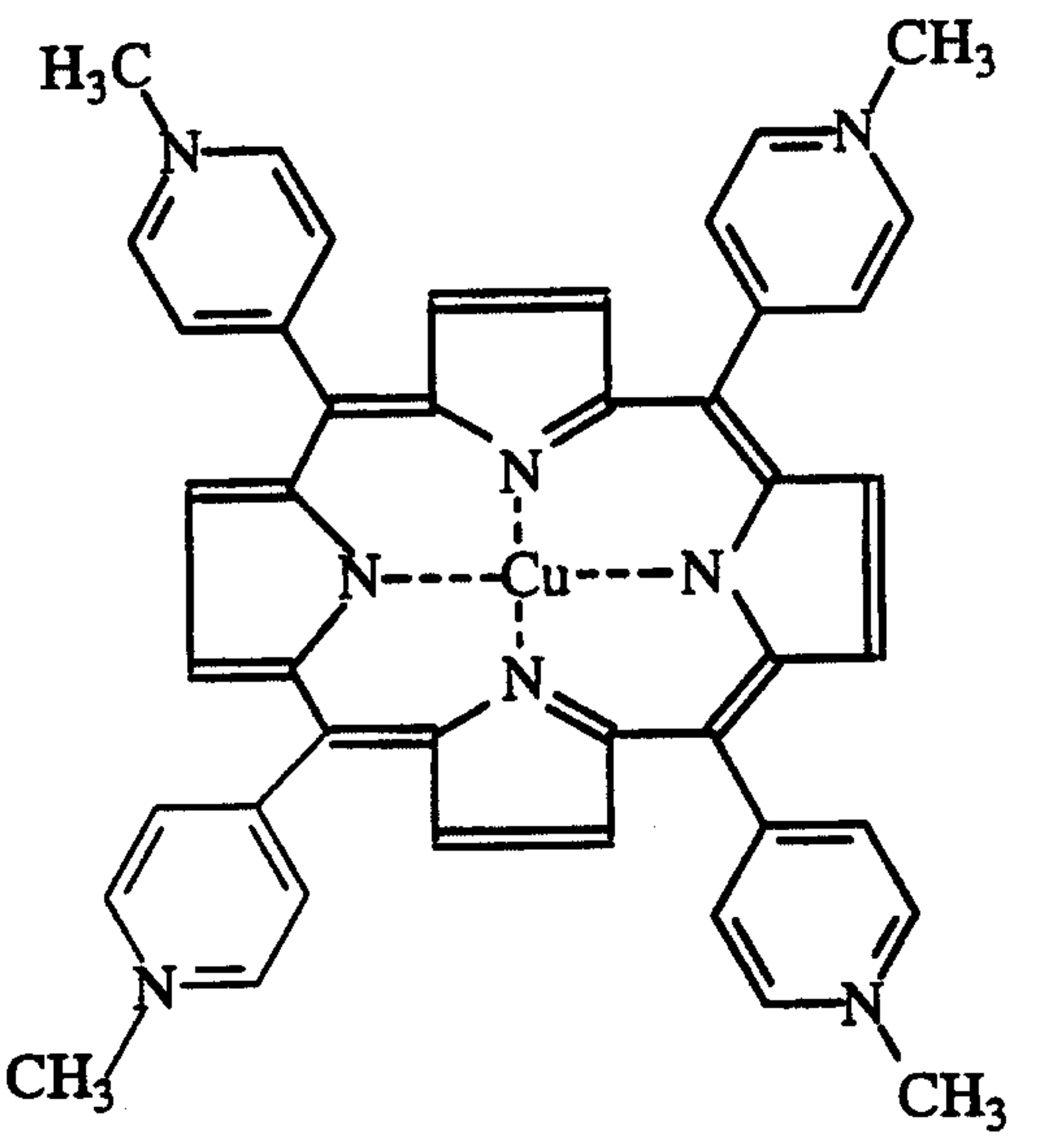
, 

, COOH, R_1COOH wherein R_1 is an alkyl group of from 1 to 6 carbons, or the corresponding salt thereof.

Desirably, the colorant stabilizer is represented by one or more porphines such as Cu-meso-tetra-(4-sulfanatophenyl)-porphine (designated CuTPPS4) and Cu-meso-tetra-(N-methyl-4-pyridyl)-porphine (designated CuTMPS4), having the following structure:



or



In the above-described porphines, the copper ion can also be substituted with an iron or cobalt ion. It is also understood that in the case of FeTPPS4, CuTPPS4 or CoTPPS4, the sulfuric acid moieties may be substituted with salts when in solution, such as sodium salts. The colorant may be stabilized with about 0.1% to 10% wt/wt porphine, more preferably about 0.3% to 1% wt/wt porphine, and more preferably about 0.5% wt/wt porphine based on the total weight of the colorant containing solution.

In another embodiment of the present invention, the neonanoplasts contain a colorant and a colorant stabilizer in the form of a metal or metal salt, such as a lanthanide or lanthanide salt. Desirably, the amount of metal or metal salt in the colorant solution is from about 0.01% to 10% wt/wt metal, more desirably about 0.03% to 1% wt/wt metal, and more desirably about 0.05% wt/wt metal. Although lanthanides and lanthanide salts are desired metals, other metals, may also be used such as magnesium, iron, zinc, and other transition metals. To improve the solubility of the metal or metal salt in solution, metal solubility-enhancing agents may be added. Particularly useful metal solubility-enhancing agents include, but are not limited to, chelating agents, including, but not limited to, EDTA (ethylenediaminetetraacetic acid) or EGTA (ethylene glycol-bis(ß-aminoethyl ether)).

In a further embodiment of the present invention, the neonanoplasts comprise a colorant in combination with a porphine and a lanthanide, such as europium. Desirably, the amount of porphine in the colorant solution is from about 0.1% to 10% wt/wt porphine, more desirably about 0.3% to 1% wt/wt porphine, and more desirably about 0.5% wt/wt porphine. Desirably, the amount of lanthanide in the colorant solution is from about 0.01% to 10% wt/wt lanthanide, more desirably about 0.03% to 1% wt/wt lanthanide, and more desirably about 0.05% wt/wt lanthanide. Although europium and europium salts are desired lanthanides, other lanthanides, may also be used.

Although not wanting to be limited by the following hypothesis, it is theorized that, in addition to the protection provided by the polymeric membrane of the neonanoplasts, the above colorant stabilizing compounds act by quenching the excited state of a dye molecule within the neonanoplast by efficiently returning it to a ground state. This reduces the likelihood of an oxidative or other chemical reaction occurring which would render the dye chromophore colorless.

The quenching process can occur by a number of processes. One such process is referred to as the heavy atom effect (internal or external) in which atoms with a high atomic number, such as iodine, xenon and lanthanides, can effect the excited electronic transitions of the dye molecule by allowing here to fore forbidden electronic transitions to occur and by decreasing the excited state lifetimes. This effect permits the rapid return of the dye to its ground state.

Another quenching process involves back electron transfer. In this case, quenching of the excited dye molecule occurs through sequential electron transfer. The additive or quencher, and dye form an ion pair through electron donation within which back electron transfer leads to an overall deactivation of the excited energy donor, i.e., the dye.

Another quenching process involves a condition in which the quencher (additive) molecule has an excited energy state lower than the excited dye. In this case, it may be possible to transfer the excited energy to the quencher thereby allowing the dye molecule to return to its ground state. These mechanisms are more fully discussed in Chemistry and Light, Suppan, P., Published by The Royal Society of Chemistry, 1994, pgs 65 - 69.

In some embodiments of the present invention, the colorant and/or colorant stabilizer within the neonanoplast is associated with a molecular includant. The term "associated" in its broadest sense means that the colorant and/or colorant stabilizer is at least in close proximity to the molecular includant. For example, the colorant and/or colorant stabilizer may be maintained in close proximity to the molecular includant by hydrogen bonding, van der Waals forces, or the like. Alternatively, the colorant and/or colorant stabilizer may be covalently bonded to the molecular includant, although this normally is neither desired nor necessary. As a further example, the colorant and/or colorant stabilizer may be at least partially included within the cavity of the molecular includant.

The molecular includant can be inorganic or organic in nature. In certain embodiments, the chemical structure of the molecular includant is adapted to form a molecular inclusion complex. Examples of molecular includants are, by way of illustration only, clathrates or intercalates, zeolites, and cyclodextrins. Examples of cyclodextrins include, but are not limited to, a-cyclodextrin, b-cyclodextrin, g-cyclodextrin, d-cyclodextrin, hydroxypropyl b-cyclodextrin, hydroxyethyl b-cyclodextrin, hydroxyethyl a cyclodextrin, carboxymethyl a cyclodextrin, carboxymethyl b cyclodextrin, carboxymethyl g cyclodextrin, octyl succinated a cyclodextrin, octyl succinated b cyclodextrin, octyl succinated g cyclodextrin and sulfated b cyclodextrin and sulfated g-cyclodextrin (Cerestar U.S.A., Incorporated, Hammond, Indiana).

The term "derivatized cyclodextrin" as used herein means a cyclodextrin having more than two leaving groups covalently coupled to each molecule of cyclodextrin. The term "leaving group" is used herein to mean any leaving group capable of participating in a bimolecular nucleophilic substitution reaction. Examples of derivatized cyclodextrin includes, but is not limited to, hydroxypropyl b-cyclodextrin, hydroxyethyl b-cyclodextrin, hydroxyethyl a cyclodextrin, carboxymethyl a cyclodextrin, carboxymethyl b cyclodextrin, carboxymethyl g cyclodextrin, octyl succinated a cyclodextrin, octyl succinated b cyclodextrin, octyl succinated g cyclodextrin and sulfated b and g-cyclodextrin. A desired derivatized cyclodextrin is ethylhydroxy b-cyclodextrin.

A desired molecular includant is g-cyclodextrin. Another desirable molecular includant is b-cyclodextrin. In other embodiments, the molecular includant is an ethyl hydroxy b-cyclodextrin. Although not wanting to be bound by the following hypothesis, it is believed that the molecular includant inhibits the aggregation of the colorant molecule in solution. Other aggregation inhibitors that can be used in practicing the present invention are starches, pectins, amyloses, clathrates and the crown ethers. It is to be understood that the addition of derivatized cyclodextrins to a neonanoplast-forming solution for the purpose of inhibiting aggregation and/or stabilizing the dyes in the neonanoplast is considered one aspect of the present invention.

In addition to the colorant, optional colorant stabilizer, and optional molecular includant, the neonanoplasts of the present invention also may contain additional components, depending upon the application for which it is intended, as long as the additional component does not negatively effect the dye molecule. Examples of such additional components include, but are not limited to, charge carriers; stabilizers against thermal oxidation; viscoelastic properties modifiers; cross-linking agents; plasticizers; charge control additives such as a quaternary ammonium salt; flow control additives such as hydrophobic silica, zinc stearate, calcium stearate, lithium stearate, polyvinylstearate, and polyethylene powders; fillers such as calcium carbonate, clay and talc; surfactants; chelating agents; and TINUVIN® compounds; among other additives used by those having ordinary skill in the art. Charge carriers are well known to those having ordinary skill in the art and typically are polymer-coated metal particles. Desirable surfactants include, but are not limited to, C_{12} to C_{18} surfactants such as cetyl trimethyl ammonium chloride and carboxymethylamylose. TINUVIN® compounds are a class of compounds produced by Ciba-Geigy Corporation, which includes benzophenones, benzotriazoles and hindered amines. Desirable TINUVIN® compounds include, but are not limited to, 2-(2'-hydroxy-3'-*sec*-butyl-5'-*tert*-butylphenyl)-benzo-triazole, poly-(N-ß-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxy-piperidyl succinate and 2-(2'-hydroxy-3',5'-di*tert*butylphenyl)-5-chloro-benzotriazole. The identities and amounts of such additional components in the colored composition are well known to one of ordinary skill in the art.

Applications For The Neonanoplasts

The present invention is also directed to colorant compositions containing the above-described neonanoplasts. The colorant composition may comprise an aqueous or non-aqueous medium, although an aqueous medium is desirable. The colorant compositions of the present invention contain neonanoplasts, as well as, any of the above-described colorant stabilizers and additives. For example, the colorant composition may contain the above-described neonanoplasts in combination with any of the following additives: a second colorant; a colorant stabilizer, such as a porphine; a molecular includant; a pre-polymer; and any additional components as described above. The present invention is particularly useful for inks to be used in ink jet printers. Inks used in ink jet printers are described in U.S. Patent No. 5,681,380, assigned to Kimberly Clark Worldwide, Inc.

The colorant compositions of the present invention may be applied to any substrate to impart a color to the substrate. The surface tension of the neonanoplasts may be controlled to enable monolayer coatings of neonanoplasts on a substrate surface.

In one embodiment of the present invention, the colorant composition comprises neonanoplasts, a liquid medium, a pre-polymer and a photoinitiator. The colorant composition is coated onto a substrate and subsequently exposed to radiation to photocure the pre-polymer, fixing the neonanoplasts to the substrate via the polymerization of the pre-polymer. Suitable pre-polymers include, but are not limited to, acrylates, diacrylates, modified acrylates, triacrylates, pentaacrylates, methacrylates and cationic resins. Suitable photoinitiators include, but are not limited to, conventional photoinitiators, as well as, photoinitiators disclosed in U.S. Patents Nos. 5,739,175; and 6,071,979; both of which are assigned to Kimberley Clark Worldwide, Inc.

The substrates to which the neonanoplasts may be applied include, but are not limited to, paper, wood, a wood product or composite, woven fabric, nonwoven fabric, textile, plastic, glass, metal, or any other substrate that would benefit from having a neonanoplast thereon. Examples of suitable substrates are disclosed in parent U.S. Patent No. 5,855,655, assigned to

Kimberly Clark Worldwide, Inc. In one embodiment of the present invention, neonanoplasts are applied to a textile article, such as clothing. A very thin coating having a thickness of about one neonanoplast may be applied to a textile surface and subsequently fixed to the surface using a pre-polymer as described above. The resulting textile has excellent hand and drapeability, as well as, brilliant color due to the thin coating of neonanoplasts of the textile.

In another further embodiment of the present invention, neonanoplasts are present in a carrier, the nature of which is well known to those having ordinary skill in the art. For many applications, the carrier will be a polymer, typically a thermosetting or thermoplastic polymer, with the latter being the more common. Examples of suitable thermosetting and thermoplastic polymers are disclosed in parent U.S. Patent No. 5,855,655 assigned to Kimberly Clark Worldwide, Inc. One particularly suitable application is the incorporation of neonanoplasts into a polymer coating of a heat transfer product, such as is used for transferring graphic images onto clothing.

The present invention is further described by the examples which follow. Such examples, however, are not to be construed as limiting in any way either the spirit or scope of the present invention. In the examples, all parts are parts by weight unless stated otherwise.

Example 1

Preparation of Magenta Neonanoplasts

To a 500 ml round bottom flask with stirring bar was added 200 ml of hexane and 40 ml of Aerosol OT (dioctyl sodium sulfosuccinate; available from American Cyanamid). To this mixture was added 1.0 ml of an acrylamide (8 mg/ml) and N,N'-methylene bisacrylamide (Aldrich Chemical Company, Milwaukee, Wisconsin) (2 mg/ml) solution in water. To this mixture was added 20 μl of N,N,N',N'-tetramethylene diamine (Aldrich Chemical Company, Milwaukee, Wisconsin). The mixture was stirred and flushed with argon gas to remove oxygen.

In a separate container, an aqueous dye solution was prepared by adding 0.083 g of Rhodamine WT (Aldrich Chemical Company, Milwaukee, Wisconsin) to 10 ml of water and stirring for about 30 minutes. The aqueous dye mixture was then added to the reaction mixture and again flushed with argon gas for 1 hour. Then, 20 µl of a 80 mg/ml solution of ammonium persulfate was added to the flask. The reaction mixture was stirred under argon gas for 8 hours.

The hexane was then removed under reduced pressure to yield a syrupy liquid. The syrupy liquid was placed in dialysis bags (SIGMA, 10,000 MW cut off) and subjected to continuous dialysis for 2 days to remove the surfactant and any unencapsulated dye. The bags were then opened and the water removed to yield neonanoplasts in the form of a light magenta powder.

Example 2

Preparation of Higher Concentrations of Magenta Neonanoplasts

The procedure of Example 1 was repeated using three different Rhodamine WT dye concentrations.

Run	Grams of Rhodamine WT in 10 ml of Water	Moles of Rhodamine WT
1	0.25	5×10^{-4}
2	0.50	1×10^{-3}
3	1.0	1.9×10^{-3}

As the dye concentration increased, the resulting neonanoplasts had a deeper magenta color. All of the resulting neonanoplasts were filtered through a 0.45 µ filter without leaving a precipitate.

Example 3

Preparation of Neonanoplasts Using Different Dyes

The procedure of Example 1 was repeated using other dyes.

Run	Dye	Grams of Dye in 20 ml of Water	Moles of Dye
1	Victoria Blue bo	0.4	1.33×10^{-3}
2	Acid Red 52	0.3	1×10^{-3}

The resulting neonanoplasts in the form of a powder had a deep color. All of the resulting neonanoplasts were filtered through a 0.45 μ filter without leaving a precipitate.

Having thus described the invention, numerous changes and modifications thereof will be readily apparent to those having ordinary skill in the art, without departing from the spirit or scope of the invention.

CLAIMS:

1. A neonanoplast that is a spherically-shaped polymeric membrane, wherein

the average particle size of the membrane is less than 500 nm;

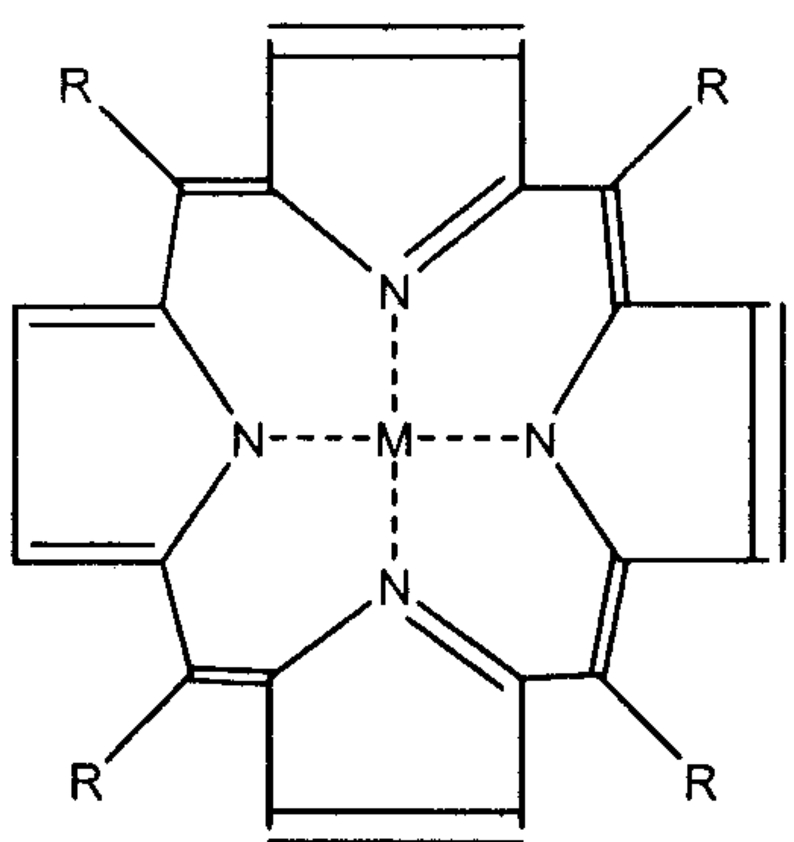
the membrane encapsulates at least one colorant;

the membrane prevents degradation of the at least one colorant;

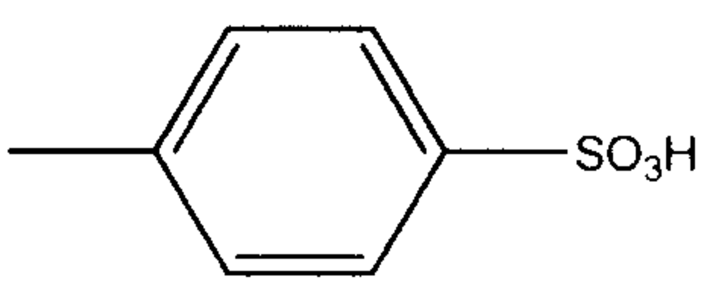
the membrane comprises at least one colorant stabilizer associated with the at least one colorant; and

the at least one colorant stabilizer is a porphine, a metal, a metal salt, a molecular includant, or a combination thereof.

2. The neonanoplast of claim 1, wherein the porphine is represented by the following formula



wherein M is iron, cobalt or copper; and wherein R is SO_3H,



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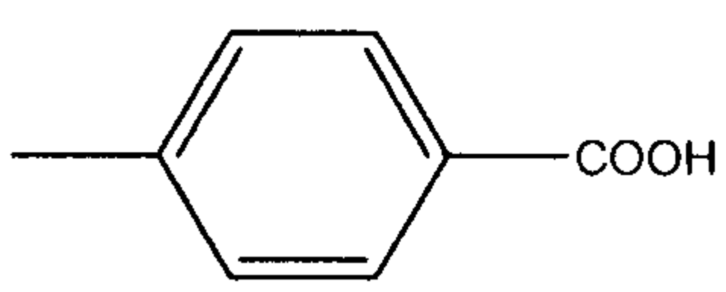

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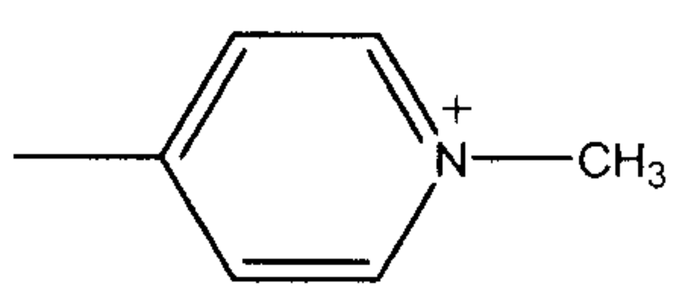
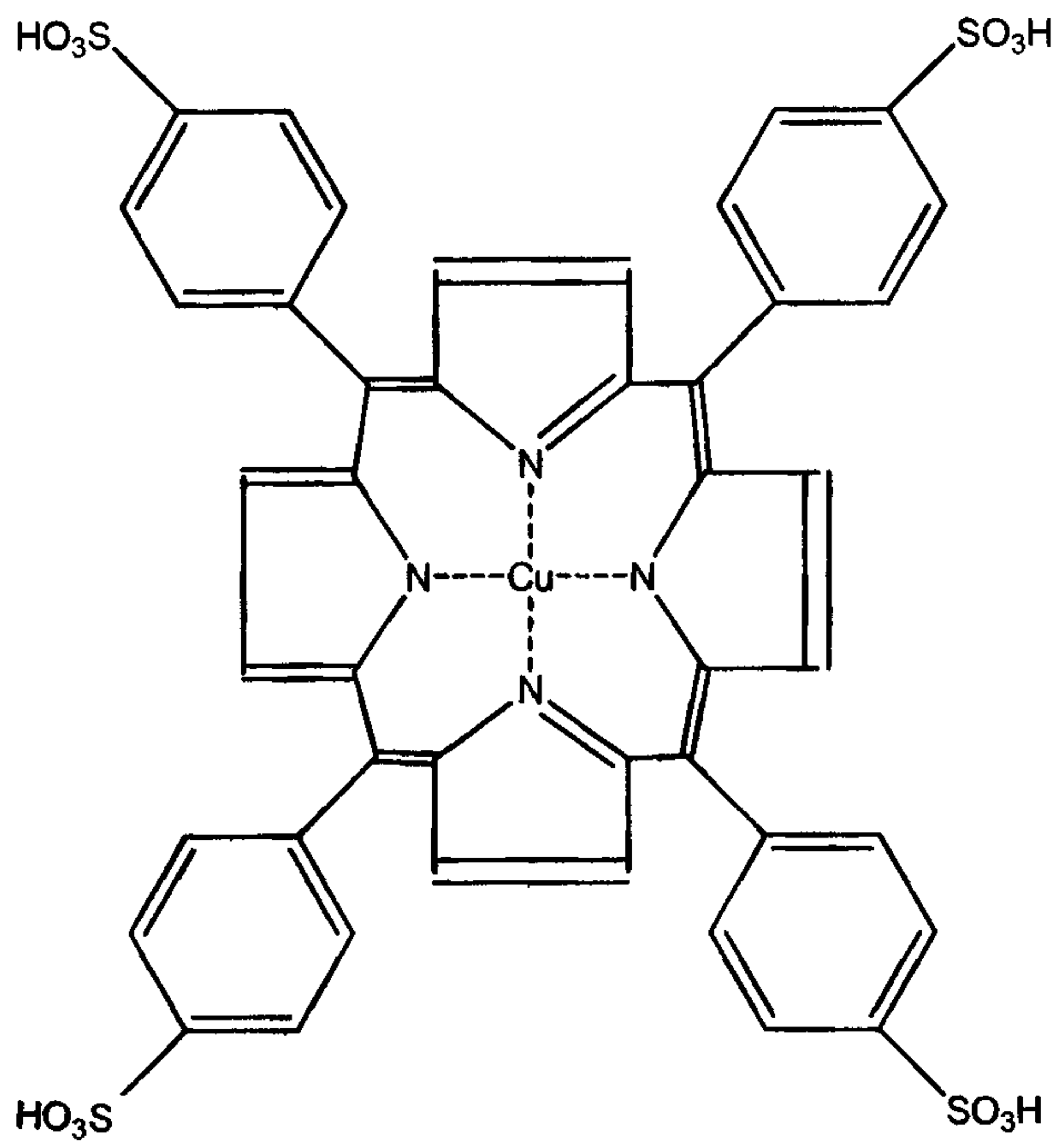


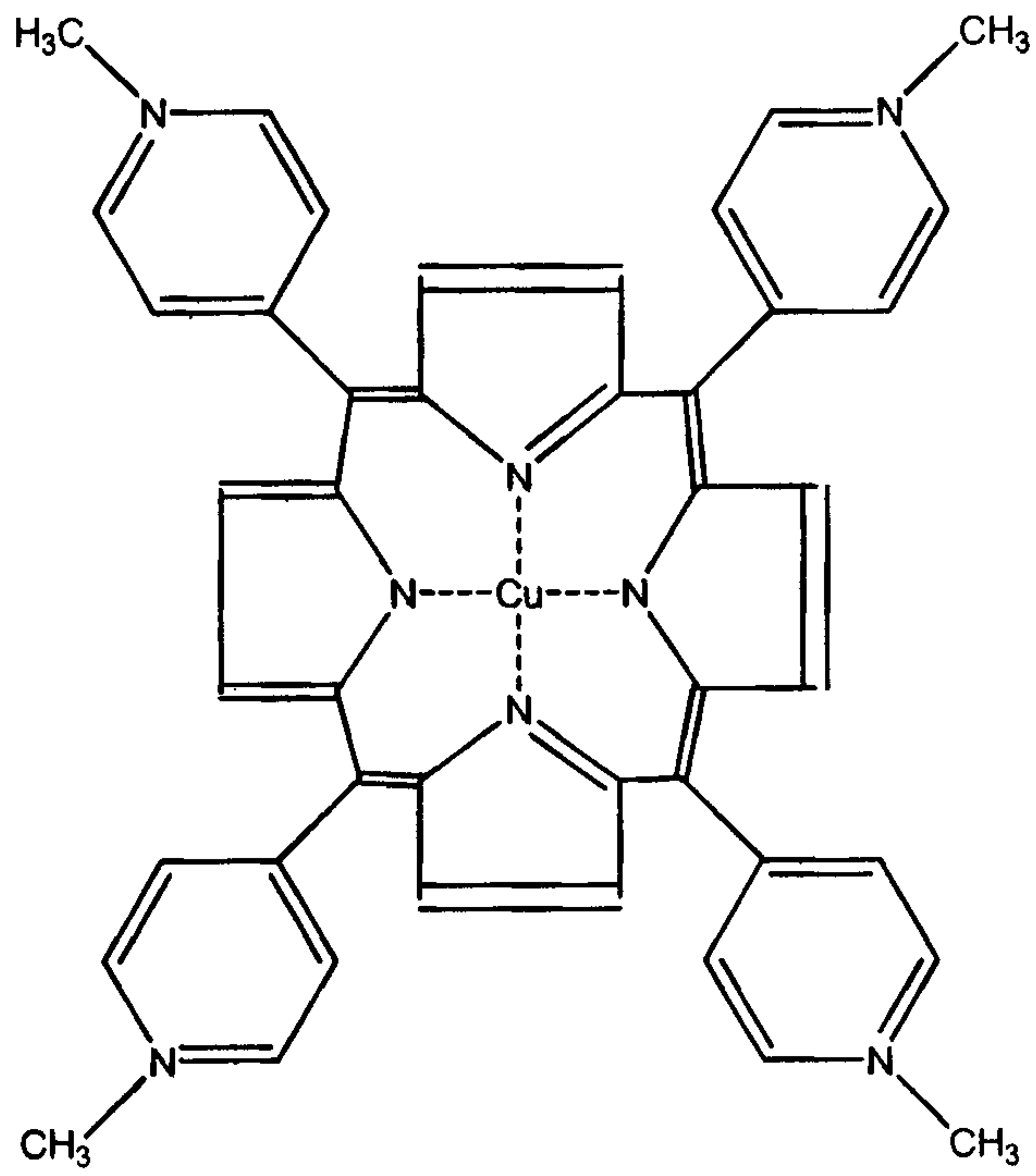
,

COOH, or R_1COOH wherein R_1 is an alkyl group of from 1 to 6 carbons.

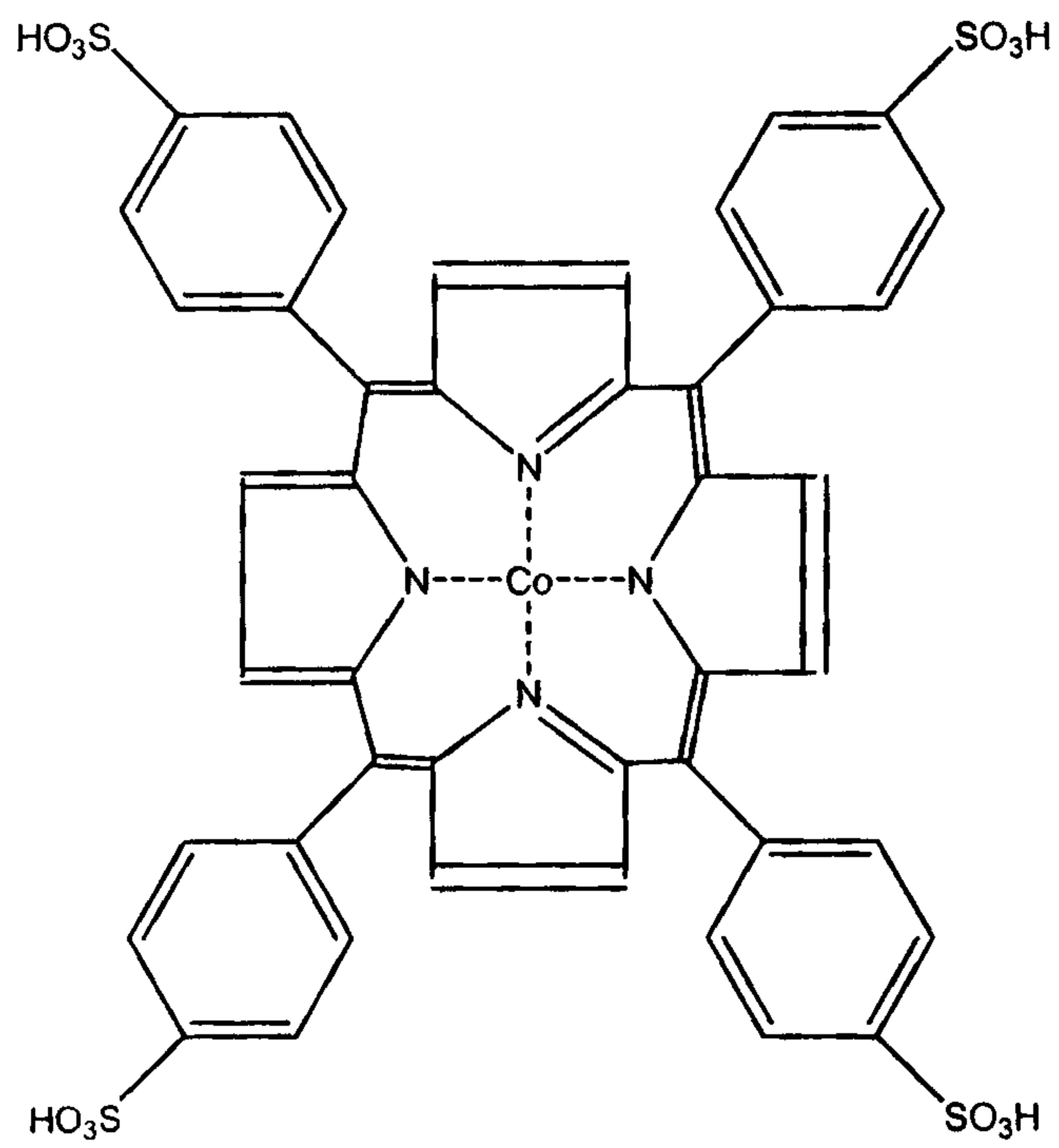
3. The neonanoplast of claim 2, wherein the porphine is Cu-meso-tetra-(4-sulfanatophenyl)-porphine or Cu-meso-tetra-(N-methyl-4-pyridyl)-porphine, having the following structures, respectively:



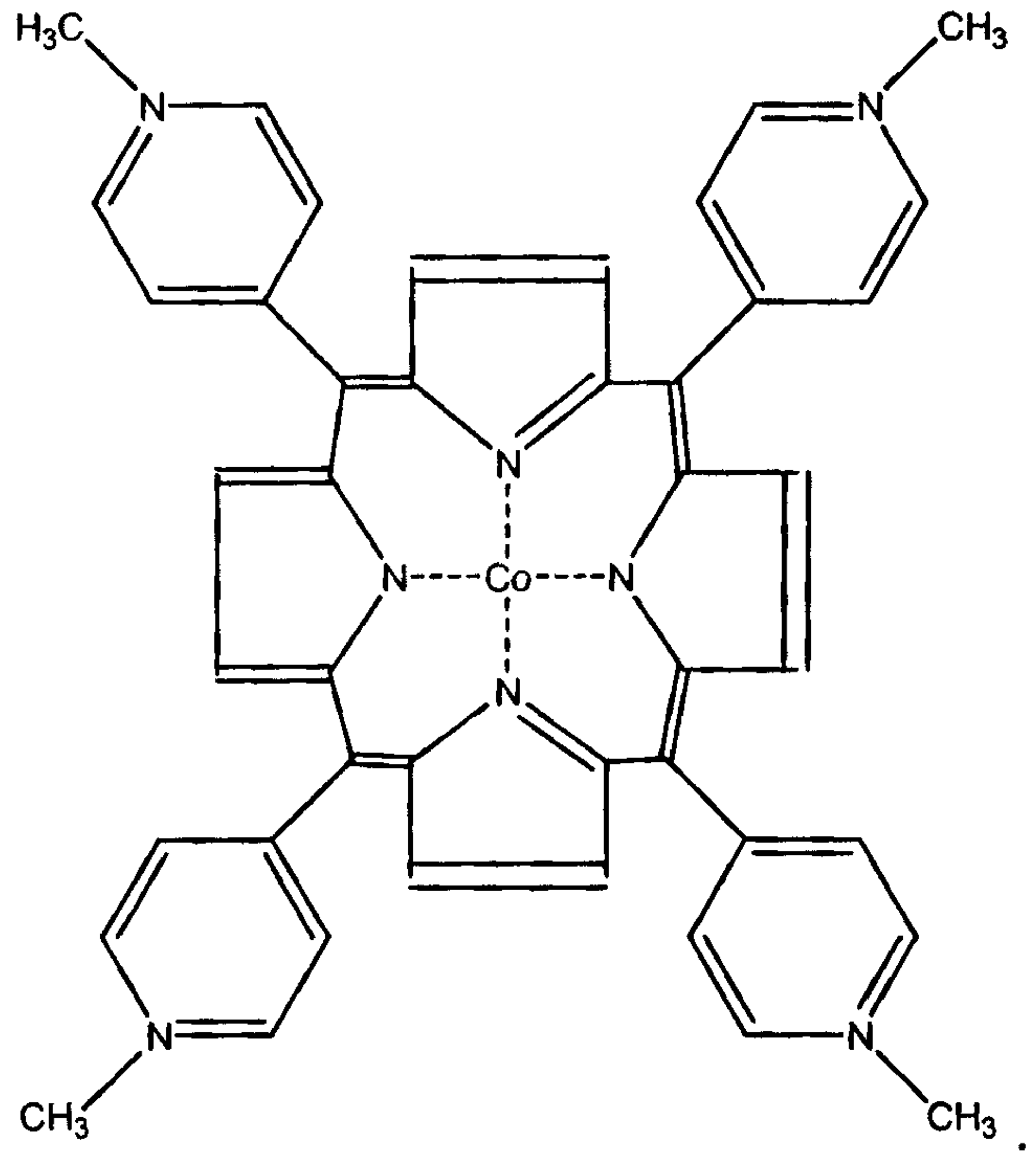
or



or the porphine is Co-meso-tetra-(4-sulfanatophenyl)-porphine or Co-meso-tetra-(N-methyl-4-pyridyl)-porphine, having the following structures, respectively:



or



4. The neonanoplast of claim 1, wherein the metal or metal salt comprises a lanthanide or lanthanide salt.

5. The neonanoplast of claim 1, wherein the molecular includant is one or more cyclodextrins.

6. The neonanoplast of claim 5, wherein the one or more cyclodextrins comprise a-cyclodextrin, b-cyclodextrin, g-cyclodextrin, d-cyclodextrin, hydroxypropyl b-cyclodextrin, or hydroxyethyl b-cyclodextrin.

7. A colorant composition comprising the neonanoplast of any one of claims 1 to 6.

8. The colorant composition of claim 7, further comprising a pre-polymer material.

9. A method of stabilizing a colorant comprising:

encapsulating the colorant in a spherically-shaped polymeric membrane to form a neonanoplast, wherein

the average particle size of the membrane is less than 500 nm;

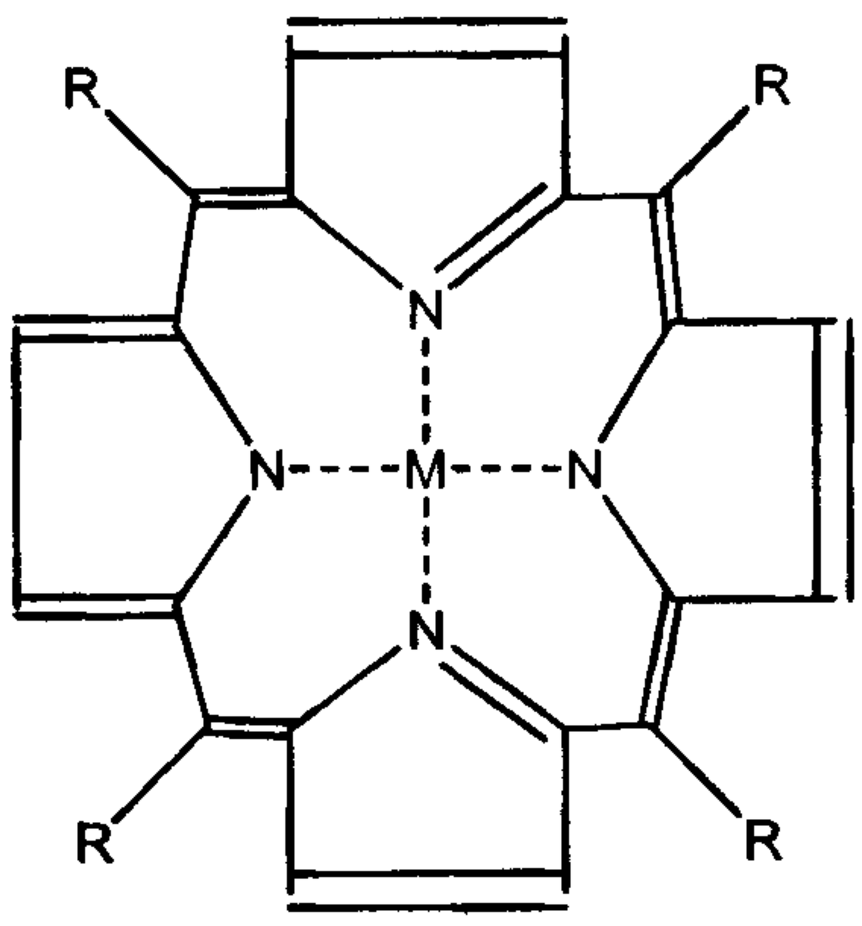
the membrane encapsulates at least one colorant;

the membrane prevents degradation of the at least one colorant;

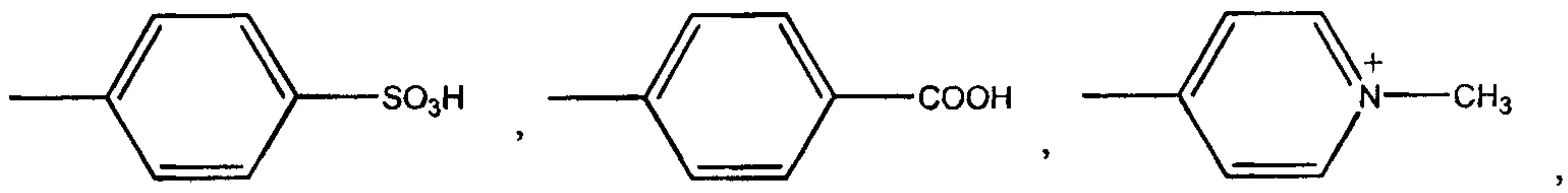
the membrane comprises at least one colorant stabilizer associated with the at least one colorant; and

the at least one colorant stabilizer is a porphine, a metal, a metal salt, a molecular includant, or a combination thereof.

10. The method of claim 9, wherein the porphine is represented by the following formula

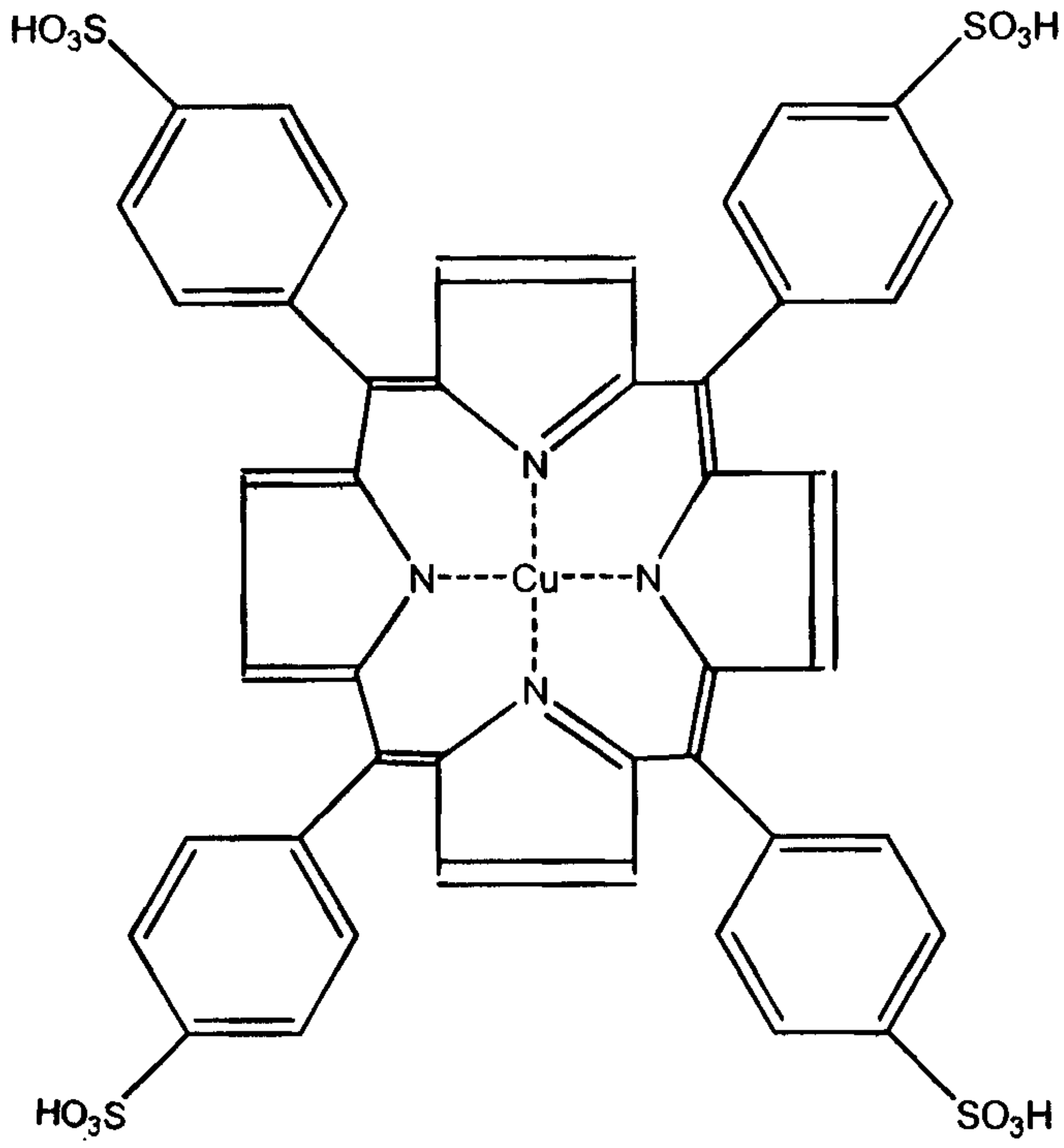


wherein M is iron, cobalt or copper; and wherein R is SO_3H,

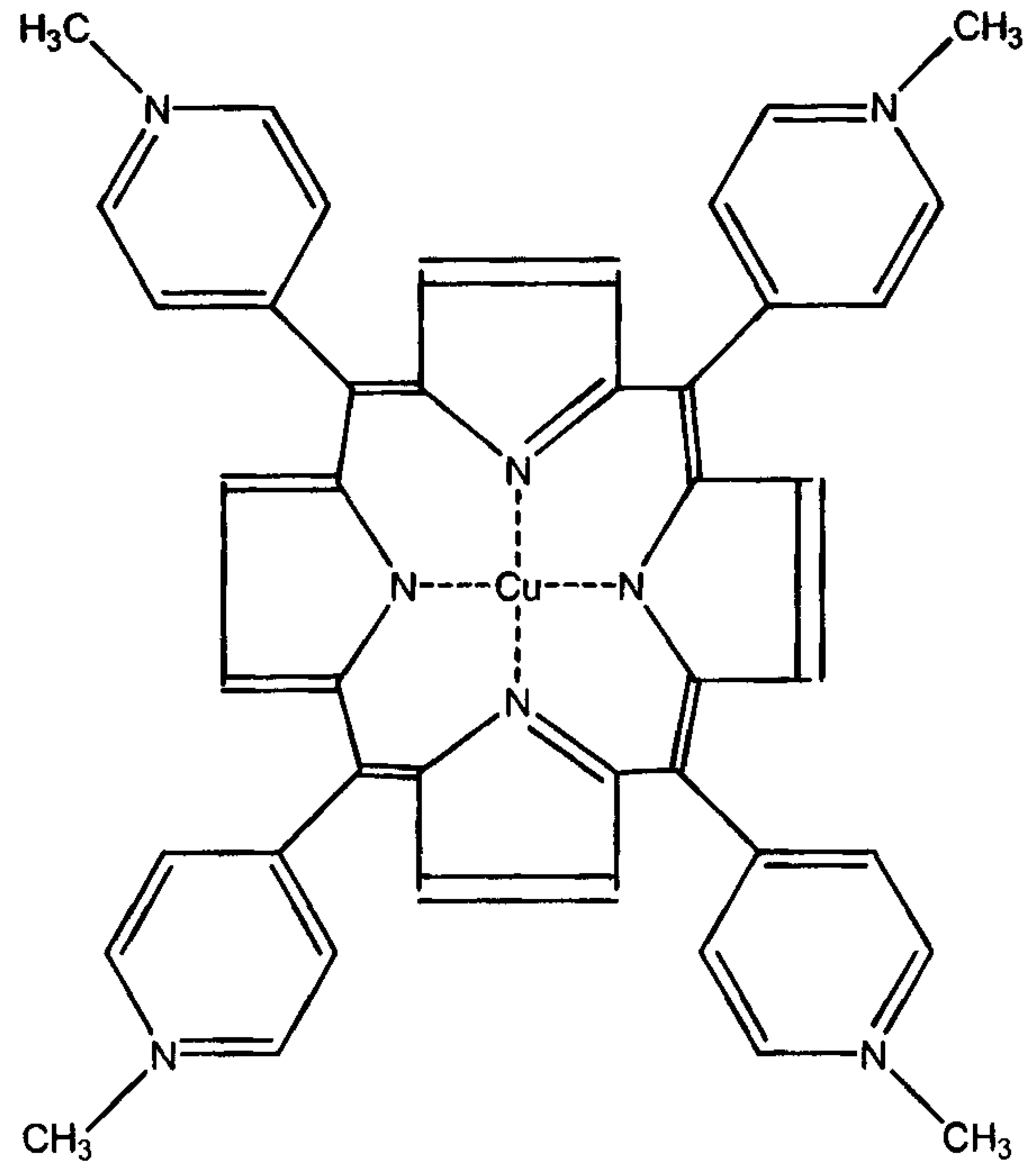


COOH, or R_1COOH wherein R_1 is an alkyl group of from 1 to 6 carbons.

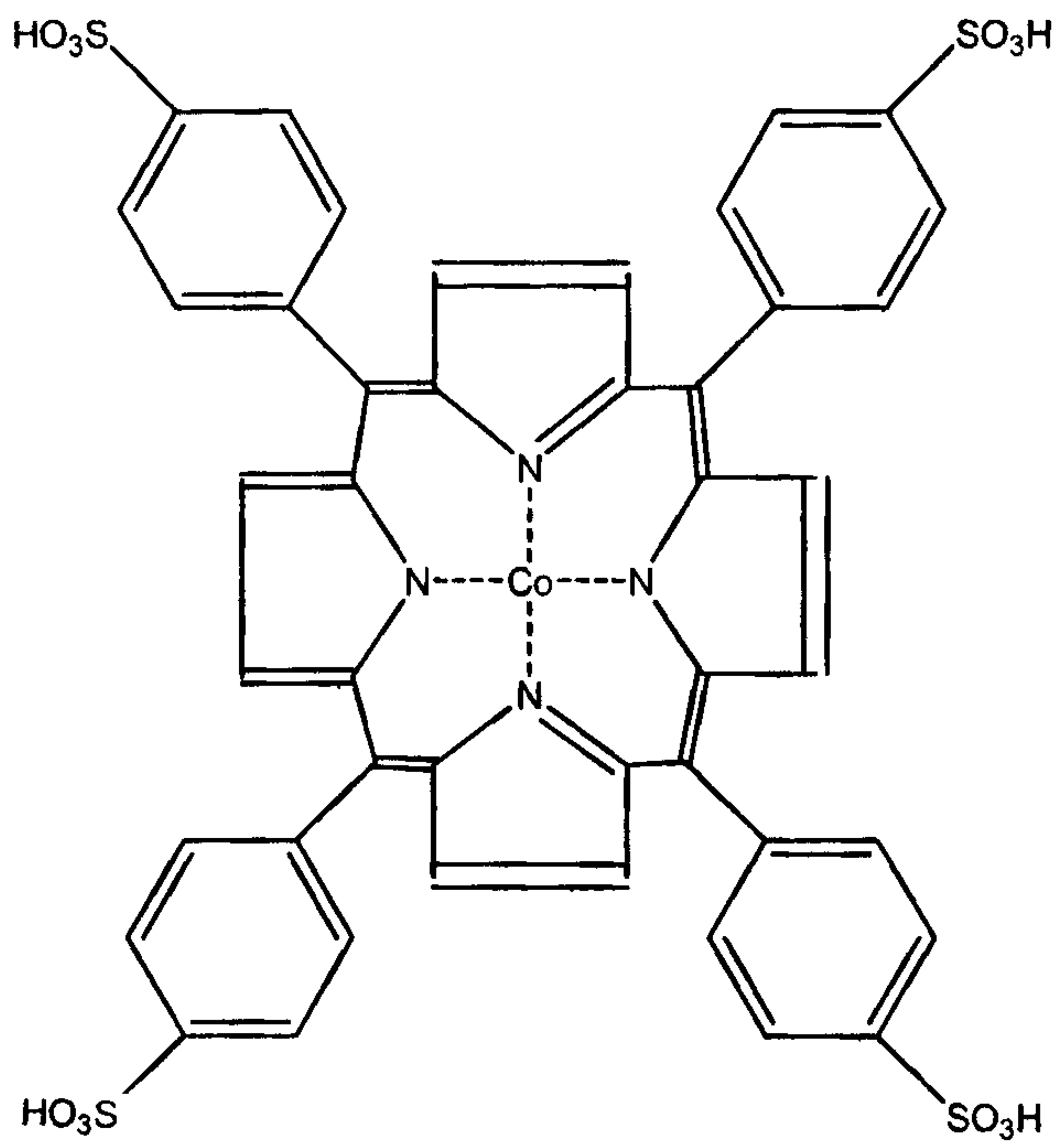
11. The method of claim 10, wherein the porphine is Cu-meso-tetra-(4-sulfanatophenyl)-porphine or Cu-meso-tetra-(N-methyl-4-pyridyl)-porphine, having the following structures, respectively:



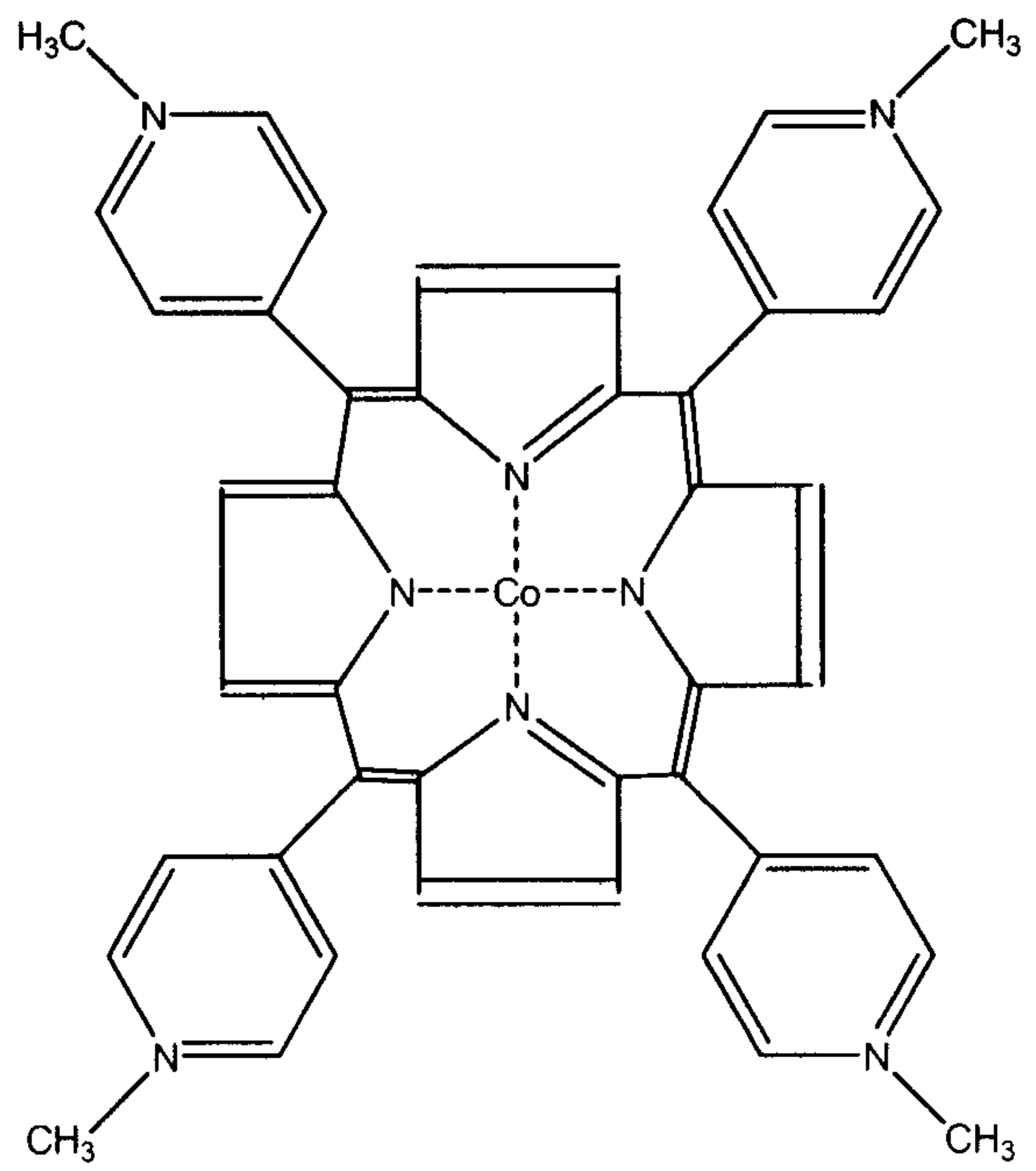
or



or the porphine is Co-meso-tetra-(4-sulfanatophenyl)-porphine or Co-meso-tetra-(N-methyl-4-pyridyl)-porphine, having the following structures, respectively:



or



12. The method of claim 9, wherein the metal or metal salt comprises a lanthanide or lanthanide salt.

13. The method of claim 9, wherein the molecular includant is one or more cyclodextrins.

14. The method of claim 13, wherein the one or more cyclodextrins comprise a-cyclodextrin, b-cyclodextrin, g-cyclodextrin, d-cyclodextrin, hydroxypropyl b-cyclodextrin, or hydroxyethyl b-cyclodextrin.

15. A method of making a colorant composition comprising:

incorporating the neonanoplasts of any one of claims 1 to 6 into a liquid medium.

16. The method of claim 15, further comprising adding a prepolymer to the colorant composition.

17. A method of forming a colored textile comprising:

coating the colorant composition of claim 8 onto a textile; and

exposing the pre-polymer to ultraviolet radiation to fix the neonanoplast to the textile.

18. A substrate having thereon or therein the neonanoplast of any one of claims 1 to 6.

19. A substrate having thereon or therein the colorant composition of claim 7 or 8.