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(71) Applicant: **SUNCOR ENERGY INC.** [CA/CA]; Suncor Energy Centre, West Tower, PO Box 2844, 150 - 6th Avenue SW, Calgary, Québec T2P 3E3 (CA).

(72) Inventors: **FEFER, Michael**; 2489 North Sheridan Way, Mississauga, Ontario L5K 1A8 (CA). **LIU, Jun**; 2489 North Sheridan Way, Mississauga, Ontario L5K 1A8 (CA). **NG, Kenneth**; 2489 North Sheridan Way, Mississauga, Ontario L5K 1A8 (CA). **TERAZONO, Yuichi**; 2489 North Sheridan Way, Mississauga, Ontario L5K 1A8 (CA). **NASH, Brady**; 2489 North Sheridan Way, Mississauga, Ontario L5K 1A8 (CA). **TESHLER, Inna**; 2489 North Sheridan Way, Mississauga, Québec L5K 1A8 (CA). **CKURSHUMOVA, Wenzi**; 2489 North Sheridan Way, Mississauga, Ontario L5K 1A8 (CA). **BROOK, Michael A.**; ABB 156, Chemistry and Chemical Biology, McMaster University, 1280 Main St. W., Hamilton, Ontario L8S 4M1 (CA). **CHEN, Yang**; ABB 156, Chemistry and Chemical Biology, McMaster University, 1280 Main St. W., Hamilton, Ontario L8S 4M1 (CA).

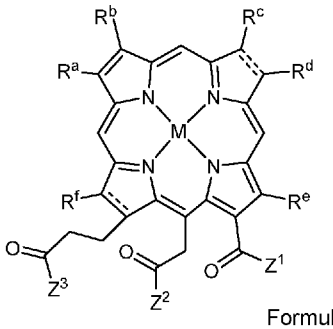
(74) Agent: **ROBIC**; 630 Rene-Levesque Boulevard West, 20th Floor, Montreal, Québec H3B 1S6 (CA).

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(54) Title: PHOTOSENSITIZER COMPOUNDS, METHODS OF MANUFACTURE AND APPLICATION TO PLANTS



Formula I

(57) Abstract: Provided herein are compounds of general Formula I: or agriculturally acceptable salts thereof. The compounds of Formula I can be used to improve the health of plants. For example, the compounds of Formula I can be used to inhibit a microbial pathogen of a plant, or to increase resistance of a plant to one or more abiotic stress. Methods of manufacturing the compounds of general Formula I, as well as synthetic intermediates are also provided.

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PHOTOSENSITIZER COMPOUNDS, METHODS OF MANUFACTURE AND APPLICATION TO PLANTS

RELATED APPLICATION

[001] This application claims priority to United-States provisional application No. 62/796,981 filed on January 25, 2019, the content of which is incorporated herein by reference in its entirety for all purposes.

FIELD

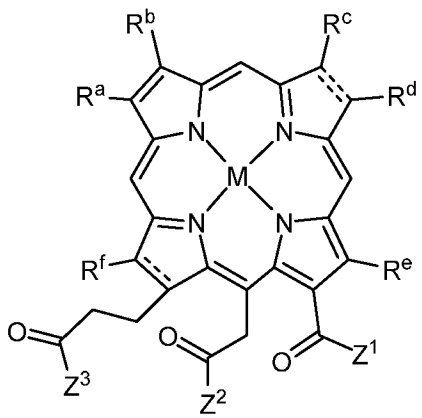
[002] The technical field generally relates to photosensitizer tetrapyrrole compounds and their use for promoting the health of plants. More particularly, the technical field relates to modified Chlorin e6 compounds and use thereof for photodynamic inhibition of microbial pathogens, such as fungal or bacterial pathogens, in plants. The modified Chlorin e6 compounds can also be used for increasing abiotic stress resistance or tolerance in plants and/or as insecticides to protect plants from plant pests.

BACKGROUND

[003] Photodynamic inhibition of microbial pathogens involves exposing a photosensitive agent to light in order to generate reactive oxygen species (ROS), such as singlet oxygen, which can have detrimental effects on the microbial pathogens. Existing photodynamic inhibition techniques and applications have various shortcomings.

SUMMARY

[004] In one aspect of the present description, there is provided a compound of Formula I:



Formula I

or an agriculturally acceptable salt thereof, for use in promoting the health of a plant, wherein:

each Z^1, Z^2 and Z^3 is independently OR^1 or NR^2R^3;

each R^1, R^2 and R^3 is independently H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, or substituted alkynyl, wherein if Z^1, Z^2 and Z^3 are each OR^1 then at least one R^1 is not H and if Z^1, Z^2 and Z^3 are each NR^2R^3 then at least one R^3 is not H;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

⎓ is a single bond or a double bond;

⎓ is a single bond or a double bond; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted aryl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more -X, $-R^B$, $-O^-$, =O, $-OR^B$, $-SR^B$, $-S^-$, $-NR^B_2$, $Si(R^C)_3$, $-N^+R^B_3$, $-NR^B$-(Alk)-NR^B_2, $-NR^B$-(Alk)-$N^+R^B_3$, $-NR^B$-(Alk)-OR^B, $-NR^B$-(Alk)-$OP(=O)(OR^B)(O^-)$, $-NR^B$-(Alk)-$OP(=O)(OR^B)_2$, $-NR^B$-(Alk)-$Si(R^C)_3$, $-NR^B$-(Alk)-SR^B, -O-(Alk)-NR^B_2, -O-(Alk)-$N^+R^B_3$, -O-(Alk)-OR^B, -O-(Alk)-$OP(=O)(OR^B)(O^-)$, -O-(Alk)-$OP(=O)(OR^B)_2$, -O-(Alk)-$Si(R^C)_3$, -O-(Alk)-SR^B, $=NR^B$, $-CX_3$, -CN, -OCN, -SCN, -N=C=O, -NCS, -NO, $-NO_2$, $=N_2$, $-N_3$, $-NHC(=O)R^B$, $-OC(=O)R^B$, $-NHC(=O)NR^B_2$, $-S(=O)_2$-, $-S(=O)_2OH$, $-S(=O)_2R^B$, $-OS(=O)_2OR^B$, $-S(=O)_2NR^B_2$, $-S(=O)R^B$, $-OP(=O)(OR^B)(O^-)$, $-OP(=O)(OR^B)_2$, $-P(=O)(OR^B)_2$, $-P(=O)(O^-)_2$, $-P(=O)(OH)_2$, $-P(O)(OR^B)(O^-)$, $-C(=O)R^B$, -C(=O)X, $-C(S)R^B$, $-C(O)OR^B$, $-C(O)O^-$, $-C(S)OR^B$, $-C(O)SR^B$, $-C(S)SR^B$, $-C(O)NR^B_2$, $-C(S)NR^B_2$ or $-C(=NR^B)NR^B_2$;

each X is independently a halogen: F, Cl, Br or I;

each R^B is independently H, alkyl, aryl, arylalkyl, a heterocycle, an alkyloxy group such as poly(ethyleneoxy), PEG or poly(methyleneoxy), a capped poly(ethyleneoxy), capped PEG or capped polymethyleneoxy, or a protecting group;

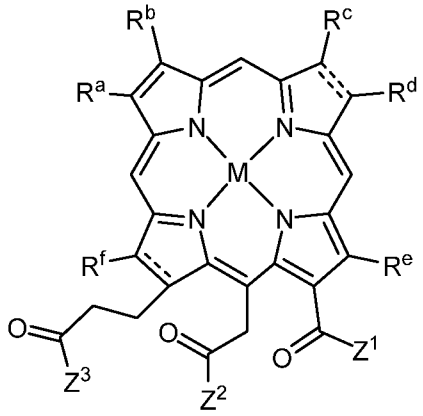
the capped poly(ethyleneoxy), capped PEG and capped poly(methyleneoxy) groups being each independently capped with alkyl, aryl, arylalkyl, alkenyl, alkynyl, CO(alkyl), CO(aryl), CO(arylalkyl), CO(alkenyl) or CO(alkynyl);

each R^C is independently alkyl, aryl, arylalkyl, O(alkyl), O(aryl), O(arylalkyl), or O(tri-substituted silyl);

each tri-substituted silyl is independently substituted with three functional groups selected from alkyl, alkenyl, alkynyl, aryl and arylalkyl; and

each Alk is independently alkylene, alkenylene, or alkynylene.

[005] In another aspect of the present description, there is provided a compound of Formula I:



Formula I

or an agriculturally acceptable salt thereof, for use in promoting the health of a plant, wherein:

Z^1 is OR^1;

one of Z^2 and Z^3 is NR^2R^3, NR^2-$(CH_2)_n$-NR^4R^5, NR^2-$(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, NR^2-$(CH_2)_n$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-SR^8, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-SR^8, OR^3, $O(CH_2)_n$-NR^4R^5, $O(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, $O(CH_2)_n$-$O(PO_3H)^-$ W^+, $O(CH_2)_n$-$Si(R^7)_3$, $O(CH_2)_n$-SR^8, $O(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+ or $O(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$; and

the other one of Z^2 and Z^3 is OR^{12};

or

Z^2 is NR^2R^3, NR^2-$(CH_2)_n$-NR^4R^5, NR^2-$(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, NR^2-$(CH_2)_n$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-SR^8, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-SR^8, OR^3, $O(CH_2)_n$-NR^4R^5, $O(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, $O(CH_2)_n$-$O(PO_3H)^-$ W^+, $O(CH_2)_n$-$Si(R^7)_3$, $O(CH_2)_n$-SR^8, $O(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+ or $O(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$; and

$Z^3 = Z^2$;

each R^1, R^2, R^4, R^6, R^8, R^9, R^{10}, R^{11} and R^{12} is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl or -$(CH_2)_q$-$(CH_2CH_2O)_m$-R^{13};

each R^3 and R^5 is, independently, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl or -$(CH_2)_q$-$(CH_2CH_2O)_m$-R^{13};

R^7 is alkyl, O(alkyl) or O(tri-substituted silyl);

R^{13} is H, alkyl, substituted alkyl, aryl, substituted aryl, CO(alkyl) or CO(substituted alkyl), alkenyl, substituted alkenyl, CO(alkenyl) or CO(substituted alkenyl), alkynyl, substituted alkynyl, CO(alkynyl) or CO(substituted alkynyl);

W^+ is an agriculturally acceptable cation;

Y^- is an agriculturally acceptable anion;

n is an integer selected from 1 to 16;

p is an integer selected from 1 to 16;

q is an integer selected from 0 to 16;

m is an integer selected from 1 to 100;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

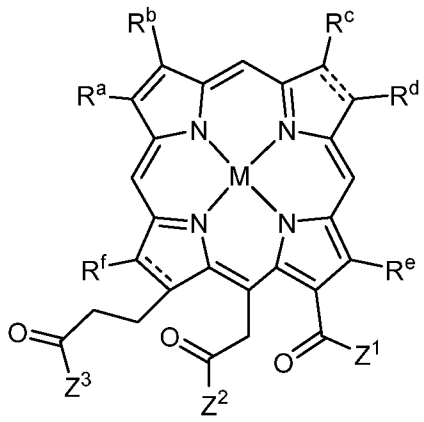
 is a single bond or a double bond;

 is a single bond or a double bond; and

M is 2H or a metal species,

wherein each substituted alkyl, substituted aryl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, CN and N_3.

[006] In yet another aspect of the present description, there is provided a compound of Formula I:



Formula I

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

one of Z^2 and Z^3 is NR^2R^3, NR^2-$(CH_2)_n$-NR^4R^5, NR^2-$(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, NR^2-$(CH_2)_n$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-SR^8, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-SR^8, $O(CH_2)_n$-NR^4R^5, $O(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, $O(CH_2)_n$-$O(PO_3H)^-$ W^+, $O(CH_2)_n$-$Si(R^7)_3$, $O(CH_2)_n$-SR^8, $O(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+ or $O(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$; and

the other one of Z^2 and Z^3 is OR^{12};

or

Z^2 is NR^2R^3, NR^2-$(CH_2)_n$-NR^4R^5, NR^2-$(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, NR^2-$(CH_2)_n$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-SR^8, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-SR^8, $O(CH_2)_n$-NR^4R^5, $O(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, $O(CH_2)_n$-$O(PO_3H)^-$ W^+, $O(CH_2)_n$-$Si(R^7)_3$, $O(CH_2)_n$-SR^8, $O(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+ or $O(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$; and

$Z^3 = Z^2$;

each R^1, R^2 and R^{12} is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

R^3 is alkyl substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

each R^4, R^6, R^8, R^9, R^{10} and R^{11} is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl or $–(CH_2)_q$-$(CH_2CH_2O)_m$-R^{13};

R^5 is alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl or -$(CH_2)_q$-$(CH_2CH_2O)_m$-R^{13};

R^7 is alkyl, O(alkyl) or O(tri-substituted silyl);

R^{13} is H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl, CO(alkyl), CO(substituted alkyl), CO(alkenyl), CO(substituted alkenyl), CO(alkynyl) or CO(substituted alkynyl);

W^+ is an agriculturally acceptable cation;

Y^- is an agriculturally acceptable anion;

n is an integer selected from 1 to 16;

p is an integer selected from 1 to 16;

m is an integer selected from 1 to 100;

q is an integer selected from 0 to 16;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

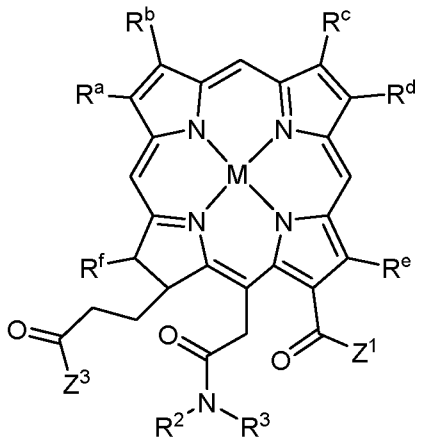
$\underline{\quad\quad}$ is a single bond or a double bond;

$\underline{\underline{\quad\quad}}$ is a single bond or a double bond; and

M is 2H or a metal species,

wherein each substituted alkyl, substituted aryl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, CN and N_3.

[007] In yet another aspect of the present description, there is provided a compound of Formula I-B1:



Formula I-B1

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

R^2 is H, alkyl or substituted alkyl;

R^3 is alkyl or substituted alkyl;

Z^3 is OR^{12} or $Z^3 = NR^2R^3$;

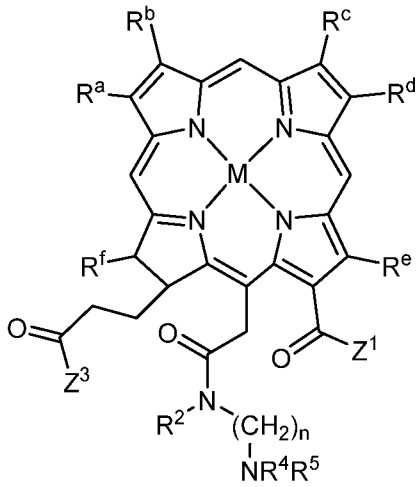
each R^1 and R^{12} is, independently, H, alkyl or substituted alkyl;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, CN and N_3.

[008] In yet another aspect of the present description, there is provided a compound of Formula I-B2:



Formula I-B2

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

R^5 is alkyl, substituted alkyl or $-(CH_2)_p-NR^9R^{10}$;

each R^2, R^4, R^9 and R^{10} is, independently, H, alkyl or substituted alkyl;

n is an integer selected from 1 to 16;

p is an integer selected from 1 to 16;

Z^3 is OR^{12} or $Z^3 = NR^2-(CH_2)_n-NR^4R^5$;

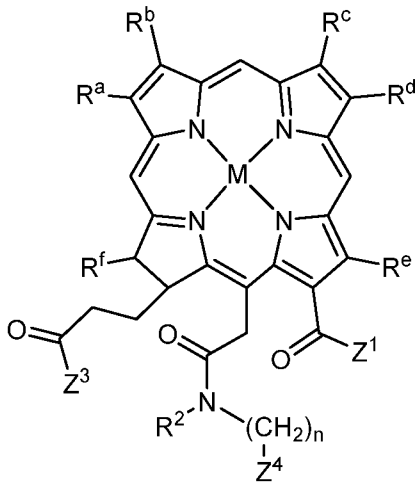
each R^1 and R^{12} is, independently, H, alkyl or substituted alkyl;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, CN and N_3.

[009] In yet another aspect of the present description, there is provided a compound of Formula I-B3:



Formula I-B3

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

Z^4 is $Si(R^7)_3$ or SR^8;

Z^3 is OR^{12} or $Z^3 = NR^2\text{-}(CH_2)_n\text{-}Z^4$;

each R^1, R^2 and R^{12} is, independently, H, alkyl or substituted alkyl;

R^7 is alkyl, O(alkyl) or O(trisubstituted silyl);

R^8 is H, alkyl, substituted alkyl or $-(CH_2CH_2O)_m\text{-}R^{13}$;

R^{13} is H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl, CO(alkyl), CO(substituted alkyl), CO(alkenyl), CO(substituted alkenyl), CO(alkynyl) or CO(substituted alkynyl);

n is an integer selected from 1 to 16;

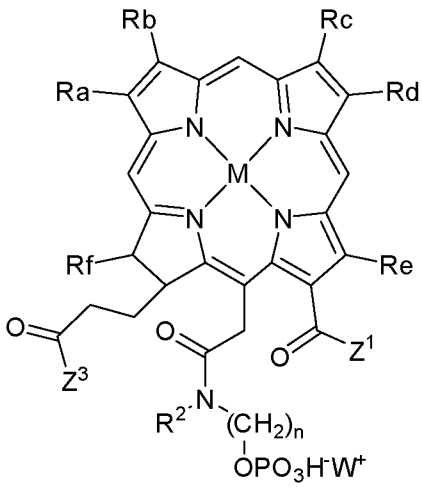
m is an integer selected from 1 to 100;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, CN and N_3.

[010] In yet another aspect of the present description, there is provided a compound of Formula I-B4a:



Formula I-B4a

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

Z^3 is OR^{12} or $Z^3 = NR_2\text{-}(CH_2)_n\text{-}O(PO_3H)^- W^+$;

each R^1, R^2 and R^{12} is, independently, H, alkyl or substituted alkyl;

n is an integer selected from 1 to 16;

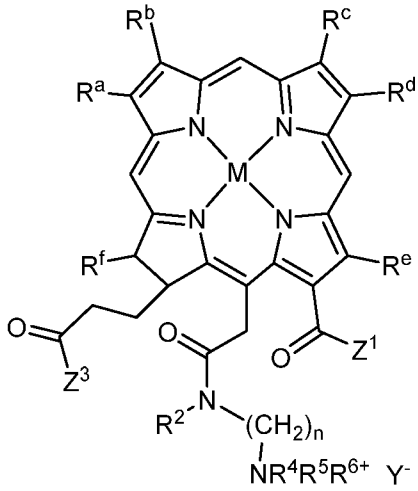
W^+ is an agriculturally acceptable cation;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, CN and N_3.

[011] In yet another aspect of the present description, there is provided a compound of Formula I-B4c:



Formula I-B4c

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

Z^3 is OR^{12} or $Z^3 = NR_2\text{-}(CH_2)_n\text{-}NR^4R^5R^{6+}\ Y^-$;

each R^1, R^2 and R^{12} is, independently, H, alkyl or substituted alkyl;

each R^4, R^5 and R^6 is, independently, alkyl or substituted alkyl;

n is an integer selected from 1 to 16;

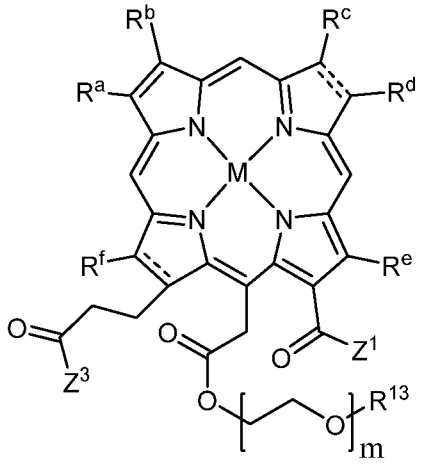
Y^- is an agriculturally acceptable anion;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, CN and N_3.

[012] In yet another aspect of the present description, there is provided a compound of Formula I-C:



Formula I-C

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

$Z^3 = OR^{12}$ and m is an integer selected from 1 to 100; or

$Z^3 = O(CH_2CH_2O)_m\text{-}R^{13}$ and m is an integer selected from 5 to 100;

each R^1 and R^{12} is, independently, H, alkyl or substituted alkyl;

R^{13} is H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl, CO(alkyl), CO(substituted alkyl), CO(alkenyl), CO(substituted alkenyl), CO(alkynyl) or CO(substituted alkynyl);

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

------ is a single bond or a double bond;

------ is a single bond or a double bond; and

M is 2H or a metal species,

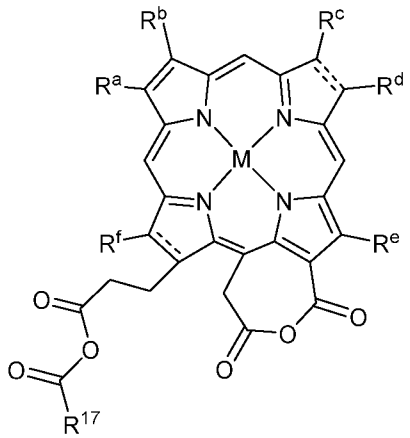
wherein the substituted alkyl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, CN and N_3.

[013] The present description also provides a composition, comprising at least one compound as defined herein, or an agriculturally acceptable salt thereof, and a carrier fluid.

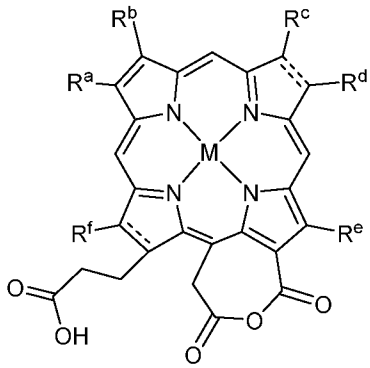
[014] The present description also provides a method for promoting the health of a plant. The method comprises applying to the plant the compound as defined herein, or an agriculturally acceptable salt thereof, or the composition as defined herein; and exposing the plant to light. Promoting the health of the plant can include at least one of preventing or inhibiting growth of a microbial pathogen of the plant (e.g., a fungus or a bacterial pathogen),

increasing resistance of the plant to one or more abiotic stress, and controlling a pest of the plant (e.g., a noxious insect or corresponding larva).

[015] The present description also provides a method of manufacturing a compound of Formula II-A and/or Formula II-B:



Formula II-A



Formula II-B

or salts thereof,

wherein:

R^{17} is H, alkyl, aryl or alkoxy;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

$\overline{\overline{\overline{\overline{\overline{\overline{\quad}}}}}}$ is a single bond or a double bond;

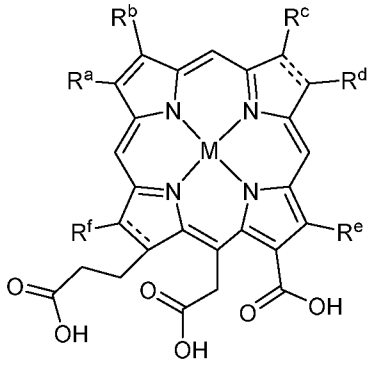
$\overline{\overline{\overline{\overline{\overline{\overline{\quad}}}}}}$ is a single bond or a double bond; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted aryl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, alkenyl, CN and N_3;

the method comprising:

reacting a compound of Formula III:



Formula III

or a salt thereof, with an anhydride of general formula $(R^{17}CO)_2O$.

BRIEF DESCRIPTION OF THE FIGURES

[016] Figure 1 is a graph showing the relative inactivation of *Erwinia amylovora* gram-negative bacteria using Ce6-mix-DMAE^{15,17} amide;

[017] Figure 2 is a graph showing the relative inactivation of *Xanthomonas axonopodis* gram-negative bacteria using Ce6-mix-DMAE^{15,17} amide;

[018] Figure 3 is a graph showing the relative inactivation of *Rhodococcus fascians* gram-positive bacteria using Ce6-mix-DMAE^{15,17} amide;

[019] Figure 4 is a graph showing comparative dose response for Ce6-mix-DMAE^{15,17} amide and Ce6Na3 under light conditions in *Pseudomonas syringae pv. tabaci* Samples;

[020] Figure 5 is a graph showing inhibition of *Colletotrichum orbiculare* ATC20767 fungus lesion formation on *Nicotiana benthamiana* host plant.

DETAILED DESCRIPTION

[021] Some microbial pathogens, such as Gram-negative bacteria and certain types of fungi have a cellular membrane that is difficult to penetrate. More specifically, these microbial pathogens sometimes have an impermeable outer cell membrane that contains endotoxins and can block small molecules such as antibiotics, dyes and detergents, thereby protecting the sensitive inner membrane and cell wall. It can therefore be challenging to use photodynamic therapy to inhibit growth of certain microbial pathogens in plants because the photosensitizer compounds tend to not achieve good penetration inside the cell wall. It can also be challenging to increase resistance of plants to damage caused by abiotic stresses.

[022] In some scenarios, photodynamic inhibition of microbial pathogens that are present on plants can be achieved by applying a photosensitizer compound. The photosensitizer compound reacts to light by generating reactive oxygen species (ROS). In other scenarios, a photosensitizer compound can be used to increase resistance of plants to damage caused by one or more abiotic stress.

[023] Some of the compounds of the present description are photosensitizer compounds that can be derived from the chlorin e6 (hereinafter "Ce6") scaffold. The compounds derived from Ce6 can also be referred to as "modified Ce6". Some of the compounds of the present description are photosensitizer compounds that have a scaffold similar to that of Ce6, but that are not necessarily derived from Ce6. In some scenarios, these compounds can be used to improve the health of plants. That is, depending on the compound and/or mode of application, the compounds of the present description can be applied to plants to photodynamically inhibit microbial pathogens on plants, to increase resistance of plants to damage caused by one or more abiotic stress and/or to be used as insecticides.

Definitions

[024] Unless stated otherwise, the following terms and phrases as used herein are intended to have the following meanings.

[025] When trade names are used herein, it is intended to independently include the tradename product and the active ingredient(s) of the tradename product.

[026] As used herein, the phrase "a compound of Formula I" means a compound of Formula I or an agriculturally acceptable salt thereof. With respect to isolatable intermediates, the phrase "a compound of Formula (number)" means a compound of that formula and salts thereof, and optionally agriculturally acceptable salts thereof.

[027] The term "Alkyl", as used herein, means a hydrocarbon containing primary, secondary, tertiary or cyclic carbon atoms. For example, and without being limiting, an alkyl group can have 1 to 20 carbon atoms (*i.e*, C_1-C_{20} alkyl), 1 to 8 carbon atoms (*i.e.*, C_1-C_8 alkyl), 1 to 6 carbon atoms (*i.e.*, C_1-C_6 alkyl) or 1 to 4 carbon atoms (*i.e.*, C_1-C_4 alkyl). Examples of suitable alkyl groups include, but are not limited to, methyl (Me, -CH_3), ethyl (Et, -CH_2CH_3), 1-propyl (*n*-Pr, *n*-propyl, -$CH_2CH_2CH_3$), 2-propyl (*i*-Pr, *i*-propyl, -$CH(CH_3)_2$), 1-butyl (*n*-Bu, *n*-butyl, -$CH_2CH_2CH_2CH_3$), 2-methyl-1-propyl (*i*-Bu, *i*-butyl, -$CH_2CH(CH_3)_2$), 2-butyl (*s*-Bu, *s*-butyl, -$CH(CH_3)CH_2CH_3$), 2-methyl-2-propyl (*t*-Bu, *t*-butyl, -$C(CH_3)_3$), 1-pentyl (*n*-

pentyl, -$CH_2CH_2CH_2CH_2CH_3$), 2-pentyl (-$CH(CH_3)CH_2CH_2CH_3$), 3-pentyl (-$CH(CH_2CH_3)_2$), 2-methyl-2-butyl (-$C(CH_3)_2CH_2CH_3$), 3-methyl-2-butyl (-$CH(CH_3)CH(CH_3)_2$), 3-methyl-1-butyl (-$CH_2CH_2CH(CH_3)_2$), 2-methyl-1-butyl (-$CH_2CH(CH_3)CH_2CH_3$), 1-hexyl (-$CH_2CH_2CH_2CH_2CH_2CH_3$), 2-hexyl (-$CH(CH_3)CH_2CH_2CH_2CH_3$), 3-hexyl (-$CH(CH_2CH_3)(CH_2CH_2CH_3)$), 2-methyl-2-pentyl (-$C(CH_3)_2CH_2CH_2CH_3$), 3-methyl-2-pentyl (-$CH(CH_3)CH(CH_3)CH_2CH_3$), 4-methyl-2-pentyl (-$CH(CH_3)CH_2CH(CH_3)_2$), 3-methyl-3-pentyl (-$C(CH_3)(CH_2CH_3)_2$), 2-methyl-3-pentyl (-$CH(CH_2CH_3)CH(CH_3)_2$), 2,3-dimethyl-2-butyl (-$C(CH_3)_2CH(CH_3)_2$), 3,3-dimethyl-2-butyl (-$CH(CH_3)C(CH_3)_3$, and octyl (-$(CH_2)_7CH_3$).

[028] The term "Alkenyl", as used herein, means a hydrocarbon containing primary, secondary, tertiary or cyclic carbon atoms with at least one site of unsaturation, *i.e.* a carbon-carbon sp^2 double bond. For example, and without being limiting, an alkenyl group can have 2 to 20 carbon atoms (*i.e.*, C_2-C_{20} alkenyl), 2 to 8 carbon atoms (*i.e.*, C_2-C_8 alkenyl), 2 to 6 carbon atoms (*i.e.*, C_2-C_6 alkenyl) or 2 to 4 carbon atoms (*i.e.*, C_2-C_4 alkenyl). Examples of suitable alkenyl groups include, but are not limited to, ethylene or vinyl (-$CH{=}CH_2$), allyl (-$CH_2CH{=}CH_2$), cyclopentenyl (-C_5H_7), and 5-hexenyl (-$CH_2CH_2CH_2CH_2CH{=}CH_2$).

[029] The term "Alkynyl", as used herein, means a hydrocarbon containing primary, secondary, tertiary or cyclic carbon atoms with at least one site of unsaturation, *i.e.* a carbon-carbon, *sp* triple bond. For example, and without being limiting, an alkynyl group can have 2 to 20 carbon atoms (*i.e.*, C_2-C_{20} alkynyl), 2 to 8 carbon atoms (*i.e.*, C_2-C_8 alkynyl), 2 to 6 carbon atoms (*i.e.*, C_2-C_6 alkynyl) or 2 to 4 carbon atoms (i.e., C_2-C_4 alkynyl). Examples of suitable alkynyl groups include, but are not limited to, acetylenic (-C≡CH) and propargyl (-CH_2C≡CH).

[030] The term "Alkoxy", as used herein, is interchangeable with the term "O(Alkyl)", in which an "Alkyl" group as defined above is attached to the parent molecule via an oxygen atom. For example, and without being limiting, the alkyl portion of an O(Alkyl) group can have 1 to 20 carbon atoms (*i.e*, C_1-C_{20} alkyl), 1 to 8 carbon atoms (*i.e.*, C_1-C_8 alkyl), 1 to 6 carbon atoms (*i.e.*, C_1-C_6 alkyl) or 1 to 4 carbon atoms (*i.e.*, C_1-C_4 alkyl). Examples of suitable Alkoxy or O(Alkyl) groups include, but are not limited to, methoxy (-OCH_3 or -OMe), ethoxy (-OCH_2CH_3 or -OEt) and *t*-butoxy (-O-$C(CH_3)_3$ or -OtBu). Similarly, "O(alkenyl)", "O(alkynyl)" and the corresponding substituted groups will be understood by a person skilled in the art.

[031] The term "Acyl", as used herein, is meant to encompass several functional moieties such as "C=O(Alkyl)", "C=O(Alkenyl)", "C=O(Alkynyl)" and their corresponding substituted

groups, in which an "Alkyl", "Alkenyl" and "Alkynyl" groups are as defined above and attached to an O, N, S of a parent molecule via a C=O group. For example, and without being limiting, the alkyl portion of a C=O(Alkyl) group can have 1 to 20 carbon atoms (*i.e*, C_1-C_{20} alkyl), 1 to 8 carbon atoms (*i.e.*, C_1-C_8 alkyl), 1 to 6 carbon atoms (*i.e.*, C_1-C_6 alkyl) or 1 to 4 carbon atoms (*i.e.*, C_1-C_4 alkyl). Examples of suitable Acyl groups include, but are not limited to, formyl (i.e., a carboxyaldehyde group), acetyl, trifluoroacetyl, propionyl, and butanoyl. A person skilled in the art will understand that a corresponding definition applies for "C=O(Alkenyl)" and "C=O(Alkynyl)" moieties. In the present description, "C=O(Alkyl)", "C=O(Alkenyl)", "C=O(Alkynyl)" can also be written as "CO(Alkyl)", "CO(Alkenyl) and "CO(Alkynyl)", respectively.

[032] The term "Alkylene", as used herein, means a saturated, branched or straight chain or cyclic hydrocarbon radical having two monovalent radical centers derived by the removal of two hydrogen atoms from the same or two different carbon atoms of a parent alkane. For example, and without being limiting, an alkylene group can have 1 to 20 carbon atoms, 1 to 10 carbon atoms, 1 to 6 carbon atoms or 1 to 4 carbon atoms. Typical alkylene radicals include, but are not limited to, methylene (-CH_2-), 1,1-ethyl (-$CH(CH_3)$-), 1,2-ethyl (-CH_2CH_2-), 1,1-propyl (-$CH(CH_2CH_3)$-), 1,2-propyl (-$CH_2CH(CH_3)$-), 1,3-propyl (-$CH_2CH_2CH_2$-) and 1,4-butyl (-$CH_2CH_2CH_2CH_2$-).

[033] The term "Alkenylene", as used herein, means an unsaturated, branched or straight chain or cyclic hydrocarbon radical having two monovalent radical centers derived by the removal of two hydrogen atoms from the same or two different carbon atoms of a parent alkene. For example, and without being limiting, and alkenylene group can have 1 to 20 carbon atoms, 1 to 10 carbon atoms, 1 to 6 carbon atoms or 1 to 4 carbon atoms. Typical alkenylene radicals include, but are not limited to, 1,2-ethylene (-CH=CH-).

[034] The term "Alkynylene", as used herein, means an unsaturated, branched or straight chain or cyclic hydrocarbon radical having two monovalent radical centers derived by the removal of two hydrogen atoms from the same or two different carbon atoms of a parent alkyne. For example, and without being limiting, an alkynylene group can have 2 to 20 carbon atoms, 2 to 10 carbon atoms, 2 to 6 carbon atoms or 2 to 4 carbon atoms. Typical alkynylene radicals include, but are not limited to, acetylene (-C≡C-), propargyl (-CH_2C≡C-), and 4-pentynyl (-$CH_2CH_2CH_2$C≡C-).

[035] The term "Aryl", as used herein, means an aromatic hydrocarbon radical derived by the removal of one hydrogen atom from a single carbon atom of a parent aromatic ring system. For example, and without being limiting, an aryl group can have 6 to 20 carbon atoms, 6 to 14 carbon atoms, or 6 to 10 carbon atoms. Typical aryl groups include, but are not limited to, radicals derived from benzene (e.g., phenyl), substituted benzene, naphthalene, anthracene and biphenyl.

[036] The term "Arylalkyl", as used herein, means an acyclic alkyl radical in which one of the hydrogen atoms bonded to a carbon atom, typically a terminal or sp^3 carbon atom, is replaced with an aryl radical. Typical arylalkyl groups include, but are not limited to, benzyl, 2-phenylethan-1-yl, naphthylmethyl, 2-naphthylethan-1-yl, naphthobenzyl, 2-naphthophenylethan-1-yl and the like. For example, and without being limiting, the arylalkyl group can include 7 to 20 carbon atoms, *e.g.*, the alkyl moiety is 1 to 6 carbon atoms and the aryl moiety is 6 to 14 carbon atoms.

[037] The term "Arylalkenyl", as used herein, means an acyclic alkenyl radical in which one of the hydrogen atoms bonded to a carbon atom, typically a terminal or sp^3 carbon atom, but also an sp^2 carbon atom, is replaced with an aryl radical. The aryl portion of the arylalkenyl can include, for example, any of the aryl groups described herein, and the alkenyl portion of the arylalkenyl can include, for example, any of the alkenyl groups described herein. The arylalkenyl group can include 8 to 20 carbon atoms, *e.g.*, the alkenyl moiety is 2 to 6 carbon atoms and the aryl moiety is 6 to 14 carbon atoms.

[038] The term "Arylalkynyl", as used herein, means an acyclic alkynyl radical in which one of the hydrogen atoms bonded to a carbon atom, typically a terminal or sp^3 carbon atom, but also an sp carbon atom, is replaced with an aryl radical. The aryl portion of the arylalkynyl can include, for example, any of the aryl groups disclosed herein, and the alkynyl portion of the arylalkynyl can include, for example, any of the alkynyl groups disclosed herein. For example, and without being limiting, the arylalkynyl group can include 8 to 20 carbon atoms, *e.g.*, the alkynyl moiety is 2 to 6 carbon atoms and the aryl moiety is 6 to 14 carbon atoms.

[039] The term "heterocycle", as used herein, means a group including a covalently closed ring wherein at least one atom forming the ring is a heteroatom. For example, and without being limiting, heterocyclic rings can be formed by three, four, five, six, seven, eight, nine, or more than nine atoms. Any number of those atoms can be heteroatoms (i.e., a heterocyclic ring can include one, two, three, four, five, six, seven, eight, nine, or more than nine

heteroatoms). In heterocyclic rings including two or more heteroatoms, those two or more heteroatoms can be the same or different from one another. Heterocycles can be substituted. Binding to a heterocycle can be at a heteroatom or via a carbon atom. It should also be understood that in the present description, the term “heterocycle” also encompasses “heteroaryl” groups.

[040] The term “protecting group”, as used herein, means a moiety of a compound that masks or alters the properties of a functional group or the properties of the compound as a whole. The chemical substructure of a protecting group can greatly vary. One function of a protecting group is to serve as an intermediate in the synthesis of the parental active substance. Chemical protecting groups and strategies for protection/deprotection are well known in the art. See: "Protective Groups in Organic Chemistry", Theodora W. Greene (John Wiley & Sons, Inc., New York, 1991).

[041] The term “substituted”, as used herein in reference to alkyl, alkylene, alkoxy, alkenyl, alkynyl, alkenylene, aryl, alkynylene, etc., for example “substituted alkyl”, “substituted alkylene”, “substituted alkoxy” – “or substituted O(Alkyl)”, “substituted alkenyl”, “substituted alkynyl”, “substituted alkenylene”, “substituted aryl” and “substituted alkynylene”, unless otherwise indicated, means alkyl, alkylene, alkoxy, alkenyl, alkynyl, alkenylene, aryl and alkynylene, respectively, in which one or more hydrogen atoms are each independently replaced with a non-hydrogen substituent.

[042] Typical non-hydrogen substituents include, but are not limited to, -X, $-R^B$, $-O^-$, =O, $-OR^B$, $-SR^B$, $-S^-$, $-NR^B_2$, $Si(R^C)_3$, $-N^+R^B_3$, $-NR^b$-(Alk)-NR^B_2, $-NR^B$-(Alk)-$N^+R^B_3$, $-NR^B$-(Alk)-OR^B, $-NR^B$-(Alk)-$OP(=O)(OR^B)(O^-)$, $-NR^B$-(Alk)-$OP(=O)(OR^B)_2$, $-NR^B$-(Alk)-$Si(R^C)_3$, $-NR^B$-(Alk)-SR^B, -O-(Alk)-NR^B_2, -O-(Alk)-$N^+R^B_3$, -O-(Alk)-OR^B, -O-(Alk)-$OP(=O)(OR^B)(O^-)$,_-O-(Alk)-$OP(=O)(OR^B)_2$, -O-(Alk)-$Si(R^C)_3$, -O-(Alk)-SR^B, $=NR^B$, $-CX_3$, -CN, -OCN, -SCN, -N=C=O, -NCS, -NO, $-NO_2$, $=N_2$, $-N_3$, $-NHC(=O)R^B$, $-OC(=O)R^B$, $-NHC(=O)NR^B_2$, $-S(=O)_2$-, $-S(=O)_2OH$, $-S(=O)_2R^B$, $-OS(=O)_2OR^B$, $-S(=O)_2NR^B_2$, $-S(=O)R^B$, $-OP(=O)(OR^B)(O^-)$, $-OP(=O)(OR^B)_2$, $-P(=O)(OR^B)_2$, $-P(=O)(O^-)_2$, $-P(=O)(OH)_2$, $-P(O)(OR^B)(O^-)$, $-C(=O)R^B$, -C(=O)X, $-C(S)R^B$, $-C(O)OR^B$, $-C(O)O^-$, $-C(S)OR^B$, $-C(O)SR^B$, $-C(S)SR^B$, $-C(O)NR^B_2$, $-C(S)NR^B_2$ or $-C(=NR^B)NR^B_2$ where each X is independently a halogen: F, Cl, Br, or I; each R^B is independently H, alkyl, aryl, arylalkyl, a heterocycle, an alkyloxy group such as poly(ethyleneoxy), PEG or poly(methyleneoxy), or a protecting group; each R^C is independently alkyl, O(alkyl) or O(tri-substituted silyl); and each Alk is independently alkylene,

substituted alkylene, alkenylene, substituted alkenylene, alkynylene or substituted alkynylene. Unless otherwise indicated, when the term "substituted" is used in conjunction with groups such as arylalkyl, which have two or more moieties capable of substitution, the substituents can be attached to the aryl moiety, the alkyl moiety, or both.

[043] Is should also be understood that the term “tri-substituted silyl” refers to a silyl group that is independently substituted with three functional groups selected from alkyl, alkenyl, alkynyl, aryl and arylalkyl. Non-limiting examples of tri-substituted silyl groups include trimethylsilyl and dimethylphenylsilyl.

[044] The term “PEG” or “poly(ethylene glycol)”, as used herein, is meant to encompass any water-soluble poly(ethylene oxide). Typically, substantially all, or all monomeric subunits are ethylene oxide subunits, though the PEG can contain distinct end capping moieties or functional groups. PEG chains of the present description can include one of the following structures: $-(CH_2CH_2O)_m-$ or $-(CH_2CH_2O)_{m-1}CH_2CH_2-$, depending on if the terminal oxygen has been displaced, where m is an integer, optionally selected from 1 to 100, 1 to 50, 1 to 30, 5 to 30, 5 to 20 or 5 to 15. The PEG can be capped with an “end capping group” that is generally a non-reactive carbon-containing group attached to a terminal oxygen or other terminal atom of the PEG. Non-limiting examples of end capping groups can include alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl, CO(alkyl), CO(substituted alkyl), CO(alkenyl), CO(substituted alkenyl), CO(alkynyl) or CO(substituted alkynyl).

[045] A person skilled in the art will recognize that substituents and other moieties of the compounds of the present description should be selected in order to provide an agriculturally useful compound which can be formulated into an acceptably stable agricultural composition that can be applied to plants. The definitions and substituents for various genus and subgenus of the compounds of the present description are described and illustrated herein. It should be understood by a person skilled in the art that any combination of the definitions and substituents described herein should not result in an inoperable species or compound. It should also be understood that the phrase “inoperable species or compound” means compound structures that violate relevant scientific principles (such as, for example, a carbon atom connecting to more than four covalent bonds) or compounds too unstable to permit isolation and formulation into agriculturally acceptable compositions.

[046] Selected substituents of the compounds of the present description can be present to a recursive degree. In this context, "recursive substituent" means that a substituent may recite another instance of itself. Because of the recursive nature of such substituents, theoretically, a large number of compounds can be present in any given implementation. For example, R^x includes a R^y substituent. R^y can be R. R can be W^3. W^3 can be W^4 and W^4 can be R or include substituents including R^y. A person skilled in the art of organic chemistry understands that the total number of such substituents is to be reasonably limited by the desired properties of the compound intended. Such properties include, by way of example and not limitation, physical properties such as molecular weight, solubility or log P, application properties such as activity against the intended target, possibility of application to plants, and practical properties such as ease of synthesis. Typically, each recursive substituent can independently occur 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, or 0, times in a given implementation. For example, each recursive substituent can independently occur 3 or fewer times in a given embodiment. Recursive substituents are an intended aspect of the compounds of the present description. A person skilled in the art of organic chemistry understands the versatility of such substituents.

[047] The term "agriculturally acceptable salt", as used herein, refers to salts that exhibit pesticidal activity (i.e., that are active against one or more biotic stress) or that can improve resistance of a plant to one or more abiotic stress. The term also refers to salts that are or can be converted in plants, water or soil to a compound or salt that exhibits pesticidal activity or that can improve resistance of a plant to one or more abiotic stress. The "agriculturally acceptable salt" can be an agriculturally acceptable cation or agriculturally acceptable anion. Non-limiting examples of agriculturally acceptable cations can include cations derived from alkali or alkaline earth metals and cations derived from ammonia and amines. For example, agriculturally acceptable cations can include sodium, potassium, magnesium, alkylammonium and ammonium cations. Non-limiting examples of agriculturally acceptable anions can include halide, phosphate, alkylsulfate and carboxylate anions. For example, agriculturally acceptable anions can include chloride, bromide, methylsulfate, ethylsulfate, acetate, lactate, dimethyl phosphate or polyalkoxylated phosphate anions.

[048] The term "optionally substituted", as used herein in reference to a particular moiety of the compounds of the present description, means a moiety wherein all substituents are hydrogen or wherein one or more of the hydrogens of the moiety can be replaced by

substituents such as those listed under the definition of the term “substituted” or as otherwise indicated.

[049] It will be understood that all enantiomers, diastereomers, and racemic mixtures, tautomers, polymorphs, and pseudopolymorphs of compounds within the scope of the formulae and compositions described herein and their agriculturally acceptable salts thereof, are embraced by the present description. All mixtures of such enantiomers and diastereomers are also within the scope of the present description.

[050] A compound of the present description and its agriculturally acceptable salts may exist as different polymorphs or pseudopolymorphs. As used herein, crystalline polymorphism means the ability of a crystalline compound to exist in different crystal structures. The crystalline polymorphism may result from differences in crystal packing (packing polymorphism) or differences in packing between different conformers of the same molecule (conformational polymorphism). As used herein, crystalline pseudopolymorphism means the ability of a hydrate or solvate of a compound to exist in different crystal structures. Pseudopolymorphs of the compounds of the present description may exist due to differences in crystal packing (packing pseudopolymorphism) or due to differences in packing between different conformers of the same molecule (conformational pseudopolymorphism). The description and depiction of the compounds of the present description is intended to include all polymorphs and pseudopolymorphs of the compounds and their agriculturally acceptable salts.

[051] A compound of the present description and its agriculturally acceptable salts may also exist as an amorphous solid. As used herein, an amorphous solid is a solid in which there is no long-range order of the positions of the atoms in the solid. The description and depiction of the compounds of the present description is intended to include all amorphous forms of the compounds and their agriculturally acceptable salts.

[052] The modifier “about” used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context. For example, the modifier “about” can include the degree of error associated with the measurement of the quantity.

[053] For agricultural use (*i.e.,* for application to plants), salts of the compounds of the present description are agriculturally acceptable salts. However, salts which are not agriculturally acceptable can also find use, for example, in the preparation or purification of

an agriculturally acceptable compound. All salts, whether or not they are agriculturally acceptable salts, are therefore to be understood as within the scope of the present description.

[054] It will be understood that the compounds described herein can be in their un-ionized, ionized, as well as zwitterionic form, and in combinations with various amounts of water (e.g., stoichiometric amounts of water) such as in hydrates.

[055] Whenever a compound described herein is substituted with more than one of the same designated group, e.g., "R^1" or "R^2", then it will be understood that the groups may be the same or different, *i.e.*, each group is independently selected. For example, in the expression "$Si(OR^7)_3$ with each R^7 being independently alkyl or aryl", it is understood that each R^7 can independently be selected from alkyl groups and aryl groups. $Si(OR^7)_3$ therefore includes both symmetrical groups where all three R^7 are the same and asymmetrical groups where at least one R^7 group is different from the other two R^7 groups, or where each R^7 group is different. It is also understood that this applies to all R^q or Z^q groups defined herein (e.g., q being selected from 1 to 17, from a to f or from A to C). A group "Z^1" will be understood to be necessarily the same as another group "Z^2" only when it is explicitly stated that "$Z^1 = Z^2$".

[056] The compounds described herein can also exist as tautomeric forms in certain cases. Although only one delocalized resonance structure will typically be depicted, all such forms are contemplated within the scope of the present description. For example, various tautomers can exist for the tetrapyrole ring systems described herein, and all their possible tautomeric forms are within the scope of the present description.

[057] The term "growing medium", as used herein, refers to any soil (of any composition) or soil-free (e.g., hydroponic) medium that is suitable for growing and cultivating a plant. The growing medium can further include any naturally occurring and/or synthetic substance(s) that are suitable for growing and cultivating the plant. The phrase "any surface of the growing medium" or "a surface of the growing medium", as used herein, refers to a surface that is directly exposed to natural and/or simulated light and/or weather.

[058] The term "applying", as used herein, refers to contacting a surface of the growing medium with at least one compound of the present description (e.g., combinations, compositions, solutions, emulsions including at least one compound of the present description), by any means known in the art (e.g., pouring, root bathing, soil drenching, drip

irrigation, etc.), or contacting an area that is beneath the surface of the growing medium with at least one compound of the present description (e.g., by soil injection), or any combination thereof, or directly contacting the plant with at least one compound of the present description (e.g., spraying).

[059] The term “crop plant”, as used herein, refers to a non-woody plant, which is grown, tended to, and harvested in a cycle of one year or less as source of foodstuffs and/or energy. Non-limiting examples of crop plants include sugar cane, wheat, rice, corn (maize), potatoes, sugar beets, barley, sweet potatoes, cassava, soybeans, tomatoes, and legumes (beans and peas).

[060] The term “woody plant”, as used herein, refers to a woody perennial plant having a single stem or trunk, and bearing lateral branches at some distance from the ground (e.g., a tree). The woody plant can be a deciduous tree, an evergreen tree (e.g., a coniferous) or a shrub. Non-limiting examples of woody plants include maple trees, citrus trees, apple trees, pear trees, oak trees, ash trees, pine trees, and spruce trees.

[061] The term “turf grass”, as used herein, refers to a cultivated grass that provides groundcover, for example a turf or lawn that is periodically cut or mowed to maintain a consistent height. Grasses belong to the *Poaceae* family, which is subdivided into six subfamilies, three of which include common turf grasses: the *Festucoideae* subfamily of cool-season turf grasses; and the *Panicoideae* and *Eragrostoideae* subfamiles of warm-season turf grasses. A limited number of species are in widespread use as turf grasses, generally meeting the criteria of forming uniform soil coverage and tolerating mowing and traffic. In general, turf grasses have a compressed crown that facilitates mowing without cutting off the growing point. In the present context, the term "turf grass" includes areas in which one or more grass species are cultivated to form relatively uniform soil coverage, including blends that are a combination of different cultivars of the same species, or mixtures that are a combination of different species and/or cultivars.

[062] Non-limiting examples of turf grasses include: bluegrasses (e.g., Kentucky bluegrass), bentgrasses (e.g., creeping bentgrass), Redtop, fescues (e.g., red fescue), ryegrasses (e.g., annual ryegrass), wheatgrasses (e.g., crested wheatgrass), beachgrass, Brome grasses (e.g., Arizona Brome), cattails (e.g., sand cattail), Alkaligrass (Puccinellia distans), crested dog's-tail (Cynosurus cristatus), bermudagrass (Cynodon spp. such as Cynodon dactylon), hybrid bermudagrass (e.g.,tifdwarf bermudagrass), Zoysiagrasses (e.g.,

Zoysia japonica), St. Augustinegrass (e.g., Bitter Blue St. Augustinegrass), Centipedegrass (Eremochloa ophiuroides), Carpetgrass (Axonopus fissifolius), Bahiagrass (Paspalum notatum), Kikuyugrass (Pennisetum clandestinum), Buffalograss (Buchloe dactyloids), Seashore paspalum (Paspalum vaginatum), Blue Grama (Bouteloua gracilis), Black Grama (Bouteloua eriopoda), Sideoats Grama (Bouteloua curtipendula), Sporobolus spp. (e.g., Alkali Sacaton), Sand Dropseed (Sporobolus cryptandrus), Prairie Dropseed (Sporobolus heterolepis), Hordeum spp. (e.g., California Barley), Common Barley, Meadow Barley, Alopecurus spp. (e.g., Creeping Foxtail and Meadow Foxtail), Stipa spp. (e.g., Needle & Thread), Elymus spp. (e.g., Blue Wildrye), Buffelgrass (Cenchrus ciliaris), Big Quaking Grass (Briza maxima), Big Bluestem (Andropogon gerardii), Little Bluestem (Schizachyruim scoparium, Sand Bluestem (Andropogon hallii), Deergrass (Muhlenbergia rigens), Eastern Gamagrass (Tripsacum dactyloides), Galleta (Hilaria jamesii), Tufted Hairgrass (Deschampsia caespitosa), Indian Rice Grass (Oryzopsis hymenoides), Indian Grass (Sorghastrum nutans), Sand Lovegrass (Eragrostis trichodes); Weeping Lovegrass (Eragrostis curvula), California Melic (Melica californica), Prairie Junegrass (Koeleria pyramidata), Prairie Sandreed (Calamovilfa longifolia), Redtop (Agrostis alba), Reed Canarygrass (Phalaris arundinacea), Sloughgrass (Spartina pectinata), Green Sprangletop (Leptochloa dubia), Bottlebush Squirreltail (Sitanion hystrix), Panicum Switchgrass (virgatum), and Purple Threeawn (Aristida purpurea).

[063] The phrase “promoting the health of a plant”, as used herein, includes at least one of controlling a disease, condition, or injury caused by a pest of a plant and increasing abiotic stress resistance or tolerance in a plant. In other words, the phrase “promoting the health of a plant” includes at least one of “controlling infection of a plant by one or more biotic agent”, “controlling infestation of a plant by one or more insect” and “increasing resistance of a plant to one or more abiotic stress”.

[064] The phrase “controlling infection of a plant by a biotic agent”, as used herein, means to diminish, ameliorate, or stabilize the infection and/or any other existing unwanted condition or side effect that is caused by the association of a microbial pathogen or infestation of an insect on the plant. The microbial pathogen can include fungi, bacteria (gram positive or gram negative), viruses, viroids, virus-like organisms, phytoplasma, etc.

[065] The term “abiotic stress”, as used herein, refers to environmental conditions that negatively impact growth, development, yield and yield quality of crop and other plants. below optimum levels. Non-limiting examples of abiotic stresses include, for example:

photooxidative conditions, drought (water deficit), excessive watering (flooding, and submergence), extreme temperatures (chilling, freezing and heat), extreme levels of light (high and low), radiation (UV-B and UV-A), salinity due to excessive Na^+ (sodicity), chemical factors (e.g., pH), mineral (metal and metalloid) toxicity, deficiency or excess of essential nutrients, gaseous pollutants (ozone, sulfur dioxide), wind, mechanical factors, and other stressors.

[066] As used herein, the term "increasing stress resistance" (and the like) refers to an increase in the ability of a plant to survive or thrive in stress conditions. Enhanced resistance or tolerance can be specific for a particular stressor, e.g., drought, excess water, nutrient deficiency, salt, cold, shade or heat, or multiple stressors. In some scenarios, increased resistance to one or more abiotic stresses can be exemplified by the reduction in degradation of quality of the plant, as compared to an untreated plant subjected to the same stress. In other scenarios, increased resistance to one or more abiotic stress can be exemplified by maintained or improved plant quality, as compared to an untreated plant subjected to the same stress.

Photosensitizer compounds

[067] As discussed above, photosensitizer compounds can be used to enable photodynamic inhibition of biotic agents (*i.e.,* microbial pathogens and/or insects) that are present on plants. The photosensitizer compounds react to light by generating reactive oxygen species (ROS).

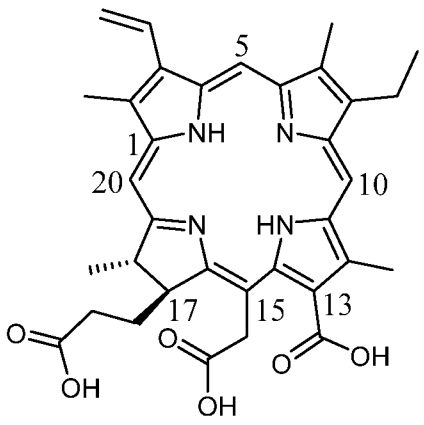
[068] Depending on the type of ROS generated, photosensitizers can be classified into two classes, namely Type I photosensitizers and Type II photosensitizers. On the one hand, Type I photosensitizers form short lived free radicals through electron abstraction or transfer from a substrate when excited at an appropriate wavelength in the presence of oxygen. On the other hand, Type II photosensitizers form a highly reactive oxygen state known as "singlet oxygen", also referred to herein as "reactive singlet oxygen species". Singlet oxygens are generally relatively long lived and can have a large radius of action.

[069] It should be understood that the photosensitizer compound can be metallated or non-metallated. When metallated, as can be the case for various nitrogen-bearing macrocyclic compounds that are complexed with a metal, the metal can be selected to generate either a Type I or a Type II photosensitizer in response to light exposure. For example, when chlorin-

type compounds are metallated with copper, the ROS that are generated are typically Type I photosensitizers. When the same chlorin-type compounds are metallated with magnesium, the ROS that are generated are typically Type II photosensitizers. Both Type I and Type II photosensitizers can be used to enable photodynamic inhibition of biotic agents that are present on plants or to protect a plant from abiotic stress.

[070] It should be understood that the term "singlet oxygen photosensitizer", as used herein, refers to a compound that produces reactive singlet oxygen species when excited by light. In other words, the term "singlet oxygen photosensitizer" refers to a photosensitizer in which the Type II process defined above is dominant compared to the Type I process.

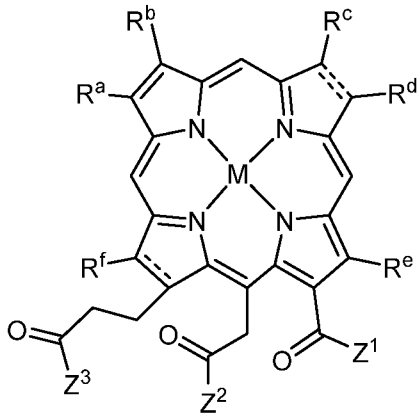
[071] Chlorin e6 (Ce6), also referred to as "phytochlorin" is represented below. Ce6 is a tetrapyrrole having a 20-carbon atom macrocyclic ring, each pyrrole being linked to two other pyrroles of the macrocyclic ring by a one-carbon bridge. It will be understood that by "tetrapyrrole", it is meant four pyrrole-like rings. As used herein, a "pyrrole-like" ring is a five-atom ring with four carbon atoms and one nitrogen atom. In the depiction of Ce6 below, the carbons of the macrocyclic ring are numbered from 1 to 20. In the chemical structure of Ce6, three carboxylic acid-bearing groups are provided at the C13 (COOH), C15 (CH_2COOH) and C17 (CH_2CH_2COOH) positions.



Chlorin e6 (Ce6)

[072] The compounds of the present description include photosensitizer compounds based on or similar to the Ce6 scaffold above, that are of general Formula I represented below, or an agriculturally acceptable salt thereof. In what follows, the term "photosensitizer compound" refers to one or more compounds of Formula I. In other words, the term "photosensitizer

compound" can refer to one compound of Formula I or to a combination or mixture of two or more compounds of Formula I.



Formula I

[073] In one aspect, there is provided a compound of Formula I, or an agriculturally acceptable salt thereof, wherein:

each Z^1, Z^2 and Z^3 is independently OR^1 or NR^2R^3;

each R^1, R^2 and R^3 is independently H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, or substituted alkynyl, wherein if Z^1, Z^2 and Z^3 are each OR^1 then at least one R^1 is not H and if Z^1, Z^2 and Z^3 are each NR^2R^3 then at least one R^3 is not H;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

$=\!=\!=\!=\!=\!=$ is a single bond or a double bond;

$=\!=\!=\!=\!=\!=$ is a single bond or a double bond; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted aryl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more -X, $-R^B$, $-O^-$, =O, $-OR^B$, $-SR^B$, $-S^-$, $-NR^B_2$, $Si(R^C)_3$, $-N^+R^B_3$, $-NR^B$-(Alk)-NR^B_2, $-NR^B$-(Alk)-$N^+R^B_3$, $-NR^B$-(Alk)-OR^B, $-NR^B$-(Alk)-$OP(=O)(OR^B)(O^-)$, $-NR^B$-(Alk)-$OP(=O)(OR^B)_2$, $-NR^B$-(Alk)-$Si(R^C)_3$, $-NR^B$-(Alk)-SR^B,

$-O$-(Alk)-NR^B_2, $-O$-(Alk)-$N^+R^B_3$, $-O$-(Alk)-OR^B, $-O$-(Alk)-$OP(=O)(OR^B)(O^-)$, $-O$-(Alk)-$OP(=O)(OR^B)_2$, $-O$-(Alk)-$Si(R^C)_3$, $-O$-(Alk)-SR^B, $=NR^B$, $-CX_3$, -CN, -OCN, -SCN, -N=C=O, -NCS, -NO, $-NO_2$, $=N_2$, $-N_3$, $-NHC(=O)R^B$, $-OC(=O)R^B$, $-NHC(=O)NR^B_2$, $-S(=O)_2$-, $-S(=O)_2OH$, $-S(=O)_2R^B$, $-OS(=O)_2OR^B$, $-S(=O)_2NR^B_2$, $-S(=O)R^B$, $-OP(=O)(OR^B)(O^-)$, $-OP(=O)(OR^B)_2$, $-P(=O)(OR^B)_2$, $-P(=O)(O^-)_2$, $-P(=O)(OH)_2$, $-P(O)(OR^B)(O^-)$, $-C(=O)R^B$,

$-C(=O)X$, $-C(S)R^B$, $-C(O)OR^B$, $-C(O)O^-$, $-C(S)OR^B$, $-C(O)SR^B$, $-C(S)SR^B$, $-C(O)NR^B_2$, $-C(S)NR^B_2$ or $-C(=NR^B)NR^B_2$;

each X is independently a halogen: F, Cl, Br or I;

each R^B is independently H, alkyl, aryl, arylalkyl, a heterocycle, an alkyloxy group such as poly(ethyleneoxy), PEG or poly(methyleneoxy), a capped poly(ethyleneoxy), capped PEG or capped polymethyleneoxy, or a protecting group;

the capped poly(ethyleneoxy), capped PEG and capped poly(methyleneoxy) groups being each independently capped with alkyl, alkenyl, alkynyl, CO(alkyl), CO(alkenyl) or CO(alkynyl);

each R^C is independently alkyl, aryl, arylalkyl, O(alkyl), O(aryl), O(arylalkyl), or O(tri-substituted silyl);

each tri-substituted silyl is independently substituted with three functional groups selected from alkyl, alkenyl, alkynyl, aryl and arylalkyl; and

each Alk is independently alkylene, alkenylene, or alkynylene.

[074] In some implementations, Z^1 is OR^1, one of Z^2 and Z^3 is NR^2R^3 and the other one of Z^2 and Z^3 is OR^1. In other implementations, Z^1 is OR^1, Z^2 is NR^2R^3 and $Z^3 = Z^2$. In some implementations, R^1 is H and/or R^2 is H, and/or R^3 is alkyl or substituted alkyl.

[075] In some implementations:

Z^1 is OR^1;

one of Z^2 and Z^3 is NR^2R^3, $NR^2\text{-}(CH_2)_n\text{-}NR^4R^5$, $NR^2\text{-}(CH_2)_n\text{-}N^+R^4R^5R^6\ Y^-$, $NR^2\text{-}(CH_2)_n\text{-}O(PO_3H)^-\ W^+$, $NR^2\text{-}(CH_2)_n\text{-}Si(R^7)_3$, $NR^2\text{-}(CH_2)_n\text{-}SR^8$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}NR^9R^{10}$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}N^+R^9R^{10}R^{11}\ Y^-$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}O(PO_3H)^-\ W^+$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}Si(R^7)_3$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}SR^8$, $O(CH_2)_n\text{-}NR^4R^5$, $O(CH_2)_n\text{-}N^+R^4R^5R^6\ Y^-$, $O(CH_2)_n\text{-}O(PO_3H)^-\ W^+$, $O(CH_2)_n\text{-}Si(R^7)_3$, $O(CH_2)_n\text{-}SR^8$, $O(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}NR^9R^{10}$, $O(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}N^+R^9R^{10}R^{11}\ Y^-$, $O(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}O(PO_3H)^-\ W^+$ or $O(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}Si(R^7)_3$; and

the other one of Z^2 and Z^3 is OR^{12};

or

Z^2 is NR^2R^3, $NR^2\text{-}(CH_2)_n\text{-}NR^4R^5$, $NR^2\text{-}(CH_2)_n\text{-}N^+R^4R^5R^6\ Y^-$, $NR^2\text{-}(CH_2)_n\text{-}O(PO_3H)^-\ W^+$, $NR^2\text{-}(CH_2)_n\text{-}Si(R^7)_3$, $NR^2\text{-}(CH_2)_n\text{-}SR^8$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}NR^9R^{10}$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}N^+R^9R^{10}R^{11}\ Y^-$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}O(PO_3H)^-\ W^+$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}Si(R^7)_3$,

NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-SR^8, $O(CH_2)_n$-NR^4R^5, $O(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, $O(CH_2)_n$-$O(PO_3H)^-$ W^+, $O(CH_2)_n$-$Si(R^7)_3$, $O(CH_2)_n$-SR^8, $O(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+ or $O(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$; and

$Z^3 = Z^2$;

each R^1, R^2 and R^{12} is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

R^3 is alkyl substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

each R^4, R^6, R^8, R^9, R^{10} and R^{11} is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl or $–(CH_2)_q$-$(CH_2CH_2O)_m$-R^{13};

R^5 is alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl or $-(CH_2)_q$-$(CH_2CH_2O)_m$-R^{13};

R^7 is alkyl, O(alkyl) or O(tri-substituted silyl);

R^{13} is H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl, CO(alkyl), CO(substituted alkyl), CO(alkenyl), CO(substituted alkenyl), CO(alkynyl) or CO(substituted alkynyl);

W^+ is an agriculturally acceptable cation;

Y^- is an agriculturally acceptable anion;

n is an integer selected from 1 to 16;

p is an integer selected from 1 to 16;

q is an integer selected from 0 to 16;

m is an integer selected from 1 to 100;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

------ is a single bond or a double bond;

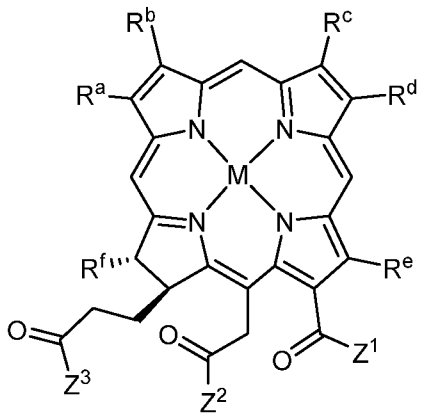
------ is a single bond or a double bond; and

M is 2H or a metal species,

wherein each substituted alkyl, substituted aryl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, CN and N_3.

[076] In some implementations, ------ is a single bond; and ------ is a double bond.

[077] In some implementations, the compound of Formula I is a compound of Formula I-A1*:



Formula I-A1*

or an agriculturally acceptable salt thereof.

[078] In some implementations, each R^a, R^b, R^c, R^d, R^e and R^f is, independently, alkyl or alkenyl. In a non-limiting example, R^a, R^c, R^e and R^f are methyl; R^b is vinyl; and R^d is ethyl.

[079] In some implementations, M is 2H. In other implementations, M is a metal species selected from the group consisting of Mg(II), Zn(II), Pd(II), Sn(IV), Al(III), Pt(II), Si(IV), Ge(IV), Ga(III) and In(III).

[080] In another aspect, there is provided a compound of Formula I, or an agriculturally acceptable salt thereof, wherein:

Z^1 is OR^1;

one of Z^2 and Z^3 is NR^2R^3, NR^2-$(CH_2)_n$-NR^4R^5, NR^2-$(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, NR^2-$(CH_2)_n$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-SR^8, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H_3)^-$ W^+, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-SR^8, OR^3, $O(CH_2)_n$-NR^4R^5, $O(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, $O(CH_2)_n$-$O(PO_3H)^-$ W^+, $O(CH_2)_n$-$Si(R^7)_3$, $O(CH_2)_n$-SR^8, $O(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+ or $O(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$; and

the other one of Z^2 and Z^3 is OR^{12};

or

Z^2 is NR^2R^3, NR^2-$(CH_2)_n$-NR^4R^5, NR^2-$(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, NR^2-$(CH_2)_n$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-SR^8, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-SR^8, OR^3, $O(CH_2)_n$-NR^4R^5, $O(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, $O(CH_2)_n$-$O(PO_3H)^-$ W^+, $O(CH_2)_n$-$Si(R^7)_3$, $O(CH_2)_n$-SR^8, $O(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+ or $O(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$; and

$Z^3 = Z^2$;

each R^1, R^2, R^4, R^6, R^8, R^9, R^{10}, R^{11} and R^{12} is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl or –$(CH_2)_q$-$(CH_2CH_2O)_m$-R^{13};

each R^3 and R^5 is, independently, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl or -$(CH_2)_q$-$(CH_2CH_2O)_m$-R^{13};

R^7 is alkyl, O(alkyl) or O(tri-substituted silyl);

R^{13} is H, alkyl, substituted alkyl, aryl, substituted aryl, CO(alkyl) or CO(substituted alkyl), alkenyl, substituted alkenyl, CO(alkenyl) or CO(substituted alkenyl), alkynyl, substituted alkynyl, CO(alkynyl) or CO(substituted alkynyl);

W^+ is an agriculturally acceptable cation;

Y^- is an agriculturally acceptable anion;

n is an integer selected from 1 to 16;

p is an integer selected from 1 to 16;

q is an integer selected from 0 to 16;

m is an integer selected from 1 to 100;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

------ is a single bond or a double bond;

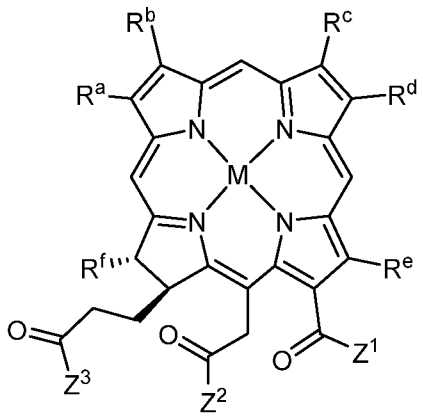
------ is a single bond or a double bond; and

M is 2H or a metal species,

wherein each substituted alkyl, substituted aryl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, CN and N_3.

[081] In some implementations, ------ is a single bond; and ------ is a double bond.

[082] In some implementations, the compound of Formula I is a compound of Formula I-A1*:



Formula I-A1*

or an agriculturally acceptable salt thereof.

[083] In some implementations, each R^a, R^b, R^c, R^d, R^e and R^f is, independently, alkyl or alkenyl. For example, and without being limiting, R^a, R^c, R^e and R^f can be methyl; R^b can be vinyl; and R^d can be ethyl.

[084] In some implementations, M is 2H. In some implementations, M is a metal species selected from the group consisting of Mg, Zn, Pd, Sn, Al, Pt, Si, Ge, Ga, In, Cu, Co, Fe and Mn. It should be understood that when a metal species is mentioned without its degree of oxidation, all suitable oxidation states of the metal species are to be considered, as would be understood by a person skilled in the art. In other implementations, M is a metal species selected from the group consisting of Mg(II), Zn(II), Pd(II), Sn(IV), Al(III), Pt(II), Si(IV), Ge(IV), Ga(III) and In(III). In yet other implementations, M is a metal species selected from the group consisting of Cu(II), Co(II), Fe(II) and Mn(II).

[085] In some implementations, each R^1, R^2, R^4, R^6, R^8, R^9, R^{10}, R^{11} and R^{12} is, independently, H, alkyl or substituted alkyl. In some implementations, each R^3 and R^5 is, independently, alkyl or substituted alkyl. In some implementations, R^{13} is H, alkyl, substituted alkyl, CO(alkyl) or CO(substituted alkyl).

[086] In some implementations, the compound is selected such that at least one of the following is true: R^1 is H, R^2 is H, R^3 is alkyl, R^4 is H or alkyl, R^5 is alkyl, R^6 is alkyl, R^7 is O(tri-substituted silyl), R^8 is $-(CH_2)_q-(CH_2CH_2O)_m-R^{13}$, R^9 is alkyl, R^{10} is alkyl, R^{11} is alkyl, R^{12} is H and R^{13} is H, alkyl, alkenyl, CO(alkyl) or CO(alkenyl).

[087] In some implementations, W^+ is selected from the group consisting of sodium, potassium, magnesium and ammonium cations. In some implementations, Y^- is selected from the group consisting of chloride, bromide, phosphate, dimethylphosphate, methylsulfate, ethylsulfate, acetate and lactate.

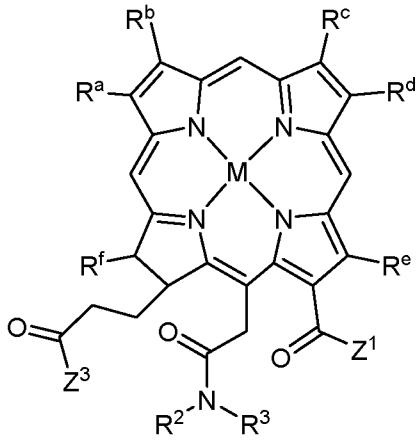
[088] In some implementations, n is an integer selected from 1 to 16, or from 1 to 12, or from 1 to 8, or from 1 to 6, or from 1 to 4, or from 2 to 4. Similarly, in some implementations, p is an integer selected from 1 to 16, or from 1 to 12, or from 1 to 8, or from 1 to 6, or from 1 to 4, or from 2 to 4. Regarding the PEG moieties, m is an integer that can be selected from 1 to 100, or from 1 to 80, or from 1 to 60, or from 1 to 50, or from 1 to 30, or from 1 to 20, or from 1 to 10, or from 5 to 30, or from 5 to 20, or from 5 to 10. Similarly, in some implementations, q is an integer selected from 0 to 16, or from 0 to 12, or from 0 to 8, or from 0 to 6, or from 0 to 4. In some implementations, q = 1. In yet other implementations, q = 0.

[089] In some implementations, Z^2 is NR^2R^3, $NR^2\text{-}(CH_2)_n\text{-}NR^4R^5$, $NR^2\text{-}(CH_2)_n\text{-}N^+R^4R^5R^6\ Y^-$, $NR^2\text{-}(CH_2)_n\text{-}O(PO_3H)^-\ W^+$, $NR^2\text{-}(CH_2)_n\text{-}Si(R^7)_3$, $NR^2\text{-}(CH_2)_n\text{-}SR^8$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}NR^9R^{10}$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}N^+R^9R^{10}R^{11}\ Y^-$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}O(PO_3H)^-\ W^+$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}Si(R^7)_3$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}SR^8$, OR^3, $O(CH_2)_n\text{-}NR^4R^5$, $O(CH_2)_n\text{-}N^+R^4R^5R^6\ Y^-$, $O(CH_2)_n\text{-}O(PO_3H)^-\ W^+$, $O(CH_2)_n\text{-}Si(R^7)_3$, $O(CH_2)_n\text{-}SR^8$, $O(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}NR^9R^{10}$, $O(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}N^+R^9R^{10}R^{11}\ Y^-$, $O(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}O(PO_3H)^-\ W^+$ or $O(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}Si(R^7)_3$; and Z^3 is OR^{12} or $Z^3 = Z^2$.

[090] In some implementations, Z^2 is NR^2R^3, $NR^2\text{-}(CH_2)_n\text{-}NR^4R^5$, $NR^2\text{-}(CH_2)_n\text{-}N^+R^4R^5R^6\ Y^-$, $NR^2\text{-}(CH_2)_n\text{-}O(PO_3H)^-\ W^+$, $NR^2\text{-}(CH_2)_n\text{-}Si(R^7)_3$, $NR^2\text{-}(CH_2)_n\text{-}SR^8$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}NR^9R^{10}$; and Z^3 is OR^{12} or $Z^3 = Z^2$.

[091] In some implementations, Z^3 is OR^{12}. For example, Z^3 can be OH. In other implementations, $Z^3 = Z^2$.

[092] In another aspect, there is provided a compound of Formula I-B1:



Formula I-B1

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

R^2 is H, alkyl or substituted alkyl;

R^3 is alkyl or substituted alkyl;

Z^3 is OR^{12} or $Z^3 = NR^2R^3$;

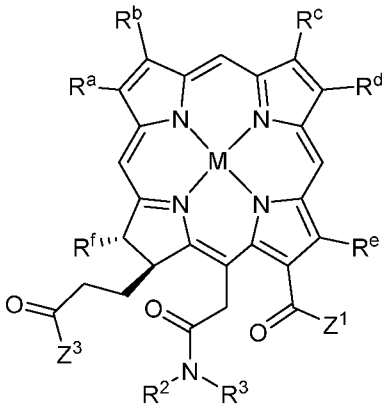
each R^1 and R^{12} is, independently, H, alkyl or substituted alkyl;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, CN and N_3.

[093] In some implementations, the compound of Formula I-B1 is a compound of Formula I-B1*:

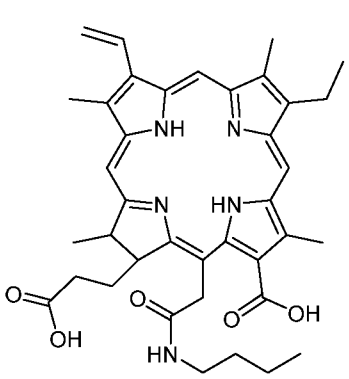
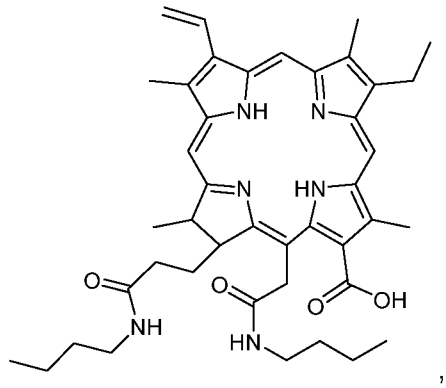
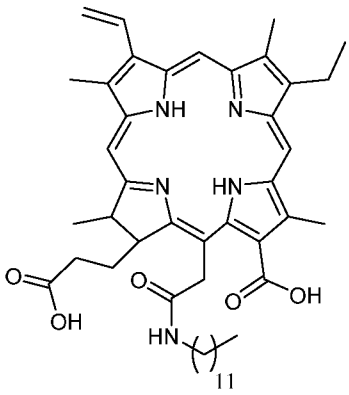
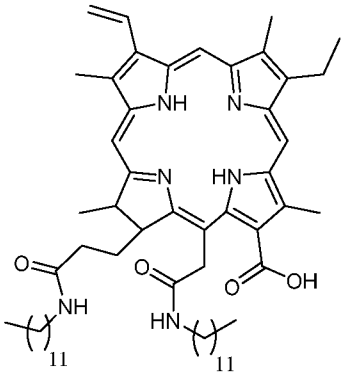
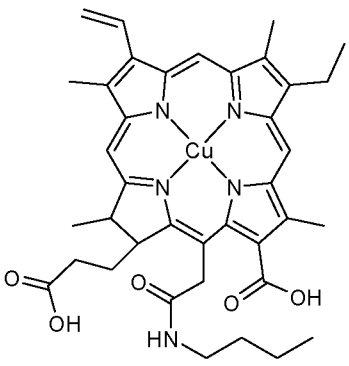
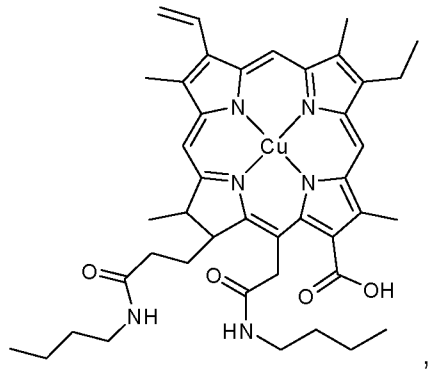


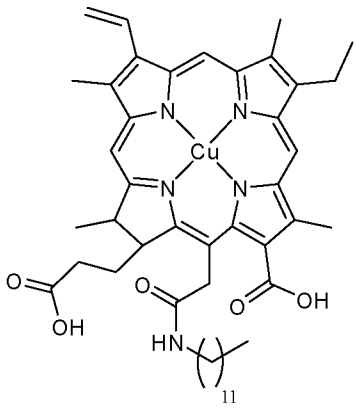
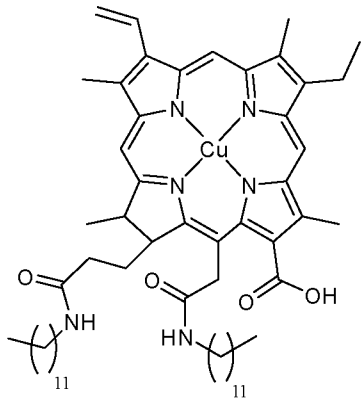
Formula I-B1*

or an agriculturally acceptable salt thereof.

[094] In some implementations, R^1 is H, R^2 is H and/or R^3 is alkyl. R^3 can for example be a (C_1-C_{12})alkyl, a (C_1-C_8)alkyl or a (C_1-C_4)alkyl. In some implementations, Z^3 is OR^{12}, and R^{12} can be H. In other implementations, $Z^3 = NR^2R^3$.

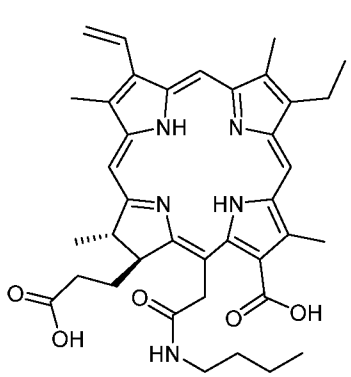
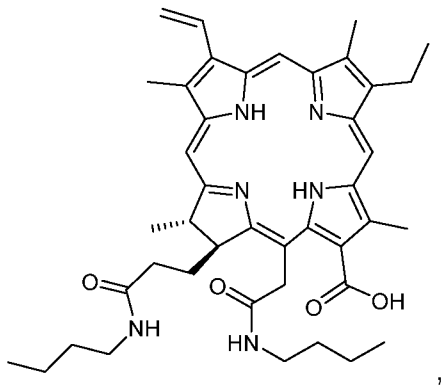
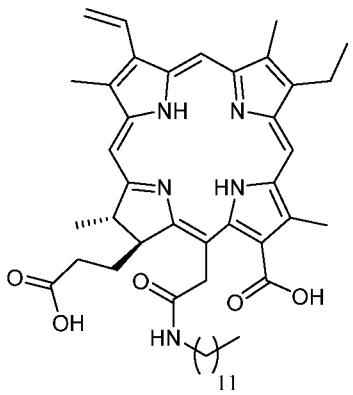
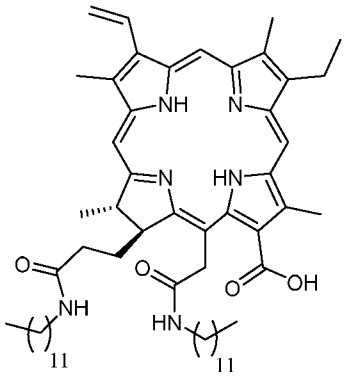
[095] In some implementations, the compound of Formula I-B1 is:

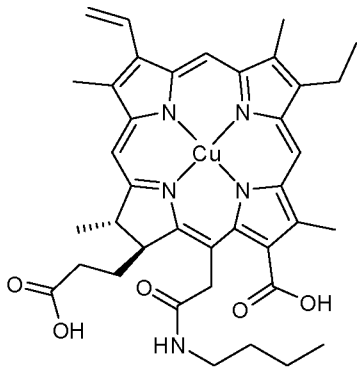







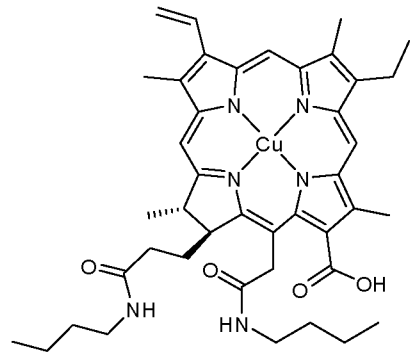
or an agriculturally acceptable salt thereof.

[096] In some implementations, the compound of Formula I-B1* is:

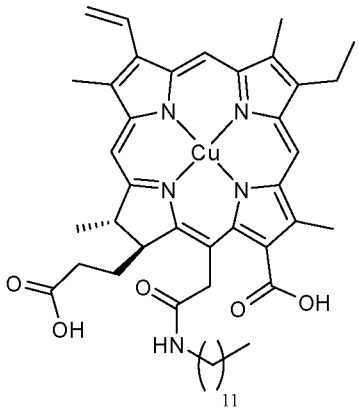







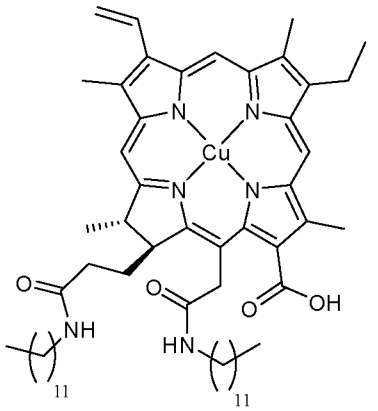
,



,



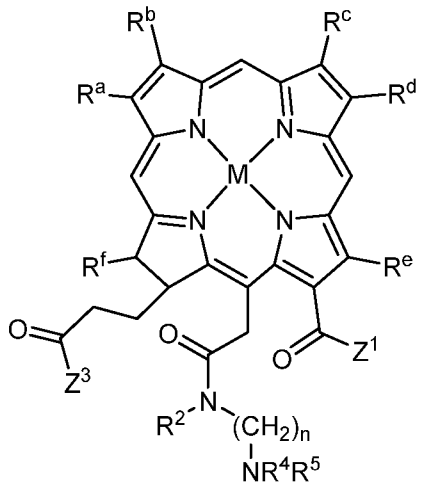
, or



,

or an agriculturally acceptable salt thereof.

[097] In another aspect, there is provided a compound of Formula I-B2:



Formula I-B2

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

R^5 is alkyl, substituted alkyl or $-(CH_2)_p-NR^9R^{10}$;

each R^2, R^4, R^9 and R^{10} is, independently, H, alkyl or substituted alkyl;

n is an integer selected from 1 to 16;

p is an integer selected from 1 to 16;

Z^3 is OR^{12} or $Z^3 = NR^2-(CH_2)_n-NR^4R^5$;

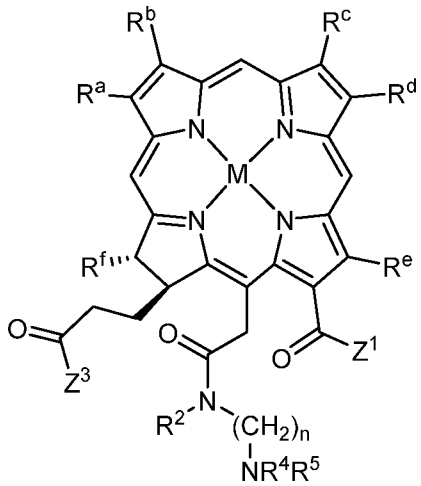
each R^1 and R^{12} is, independently, H, alkyl or substituted alkyl;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, CN and N_3.

[098] In some implementations, the compound of Formula I-B2 is a compound of Formula I-B2*:

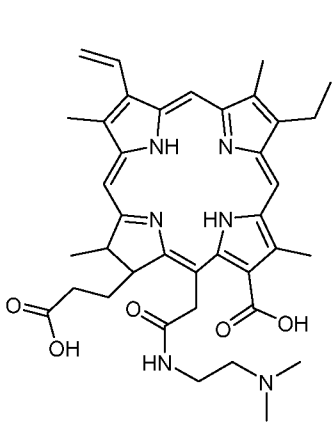
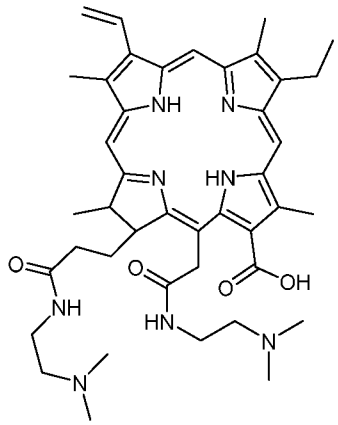
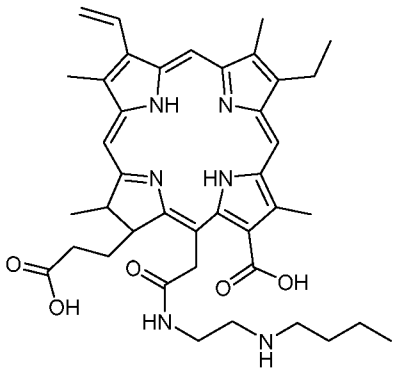
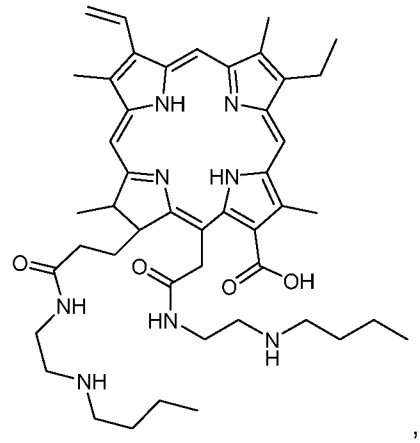
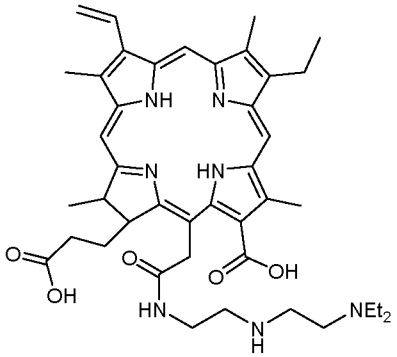
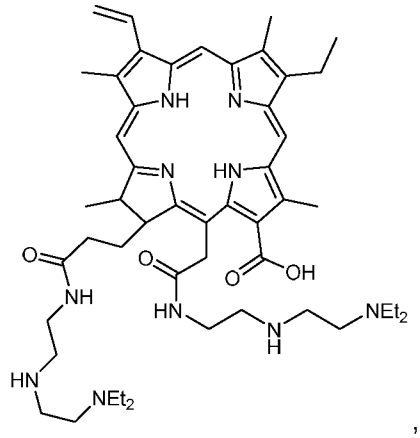
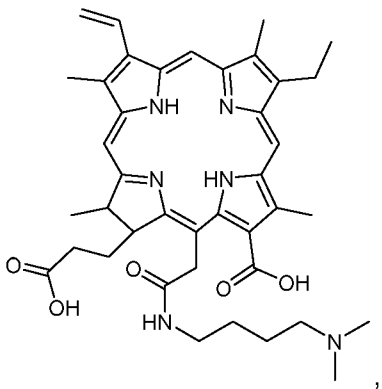
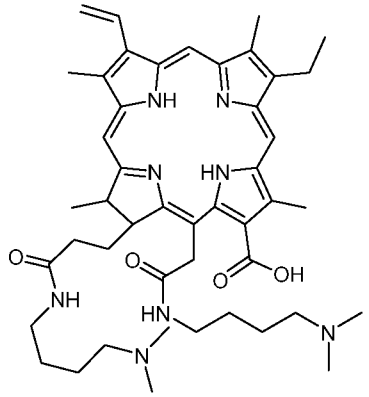


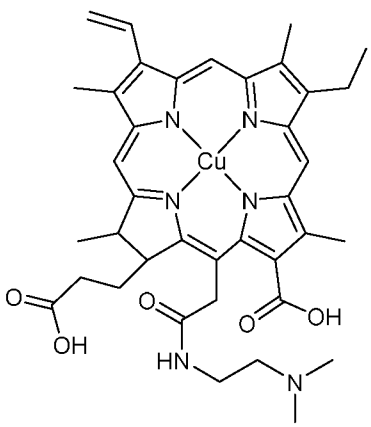
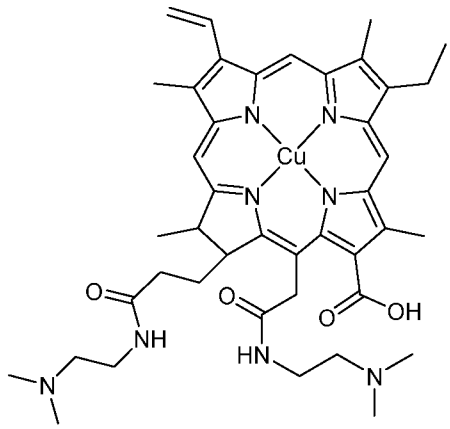
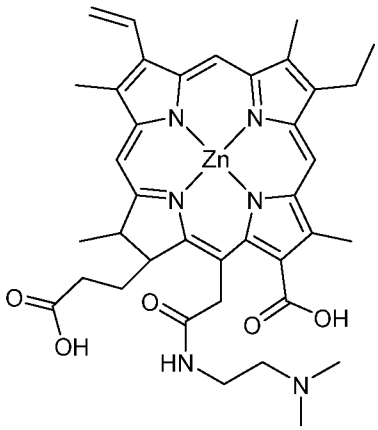
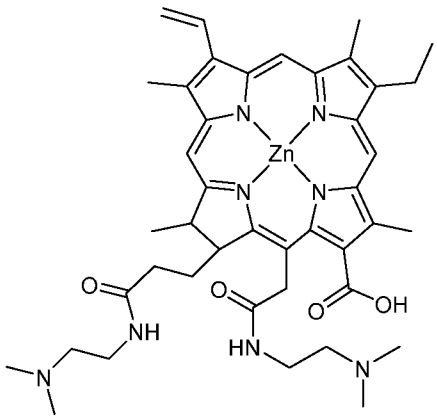
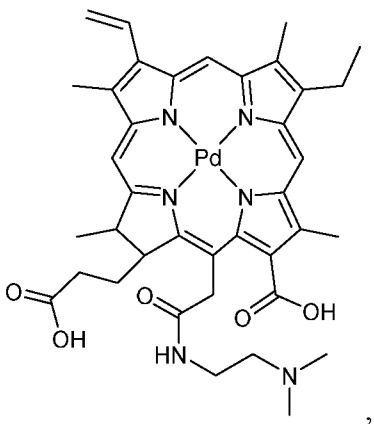
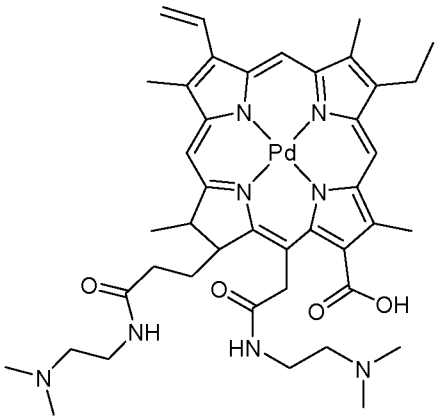
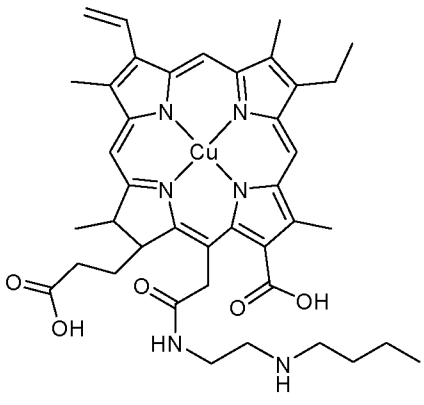
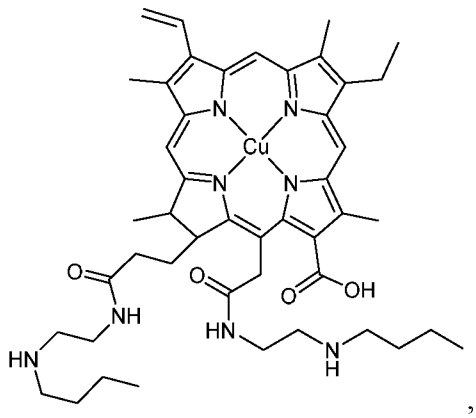
Formula I-B2*

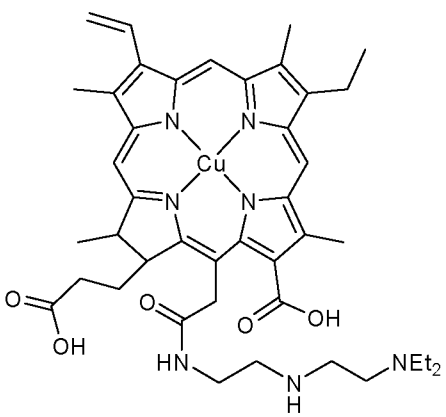
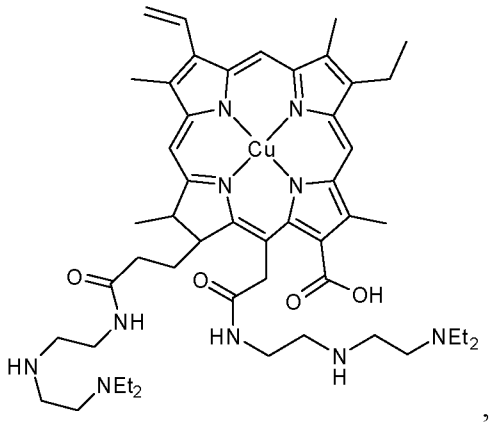
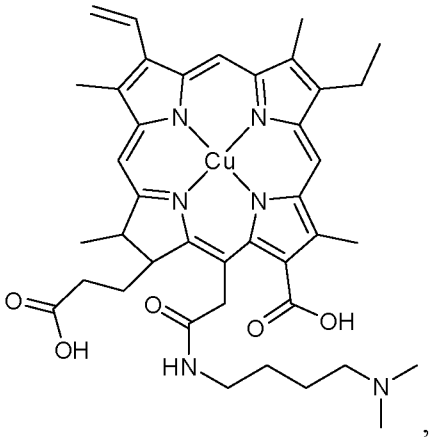
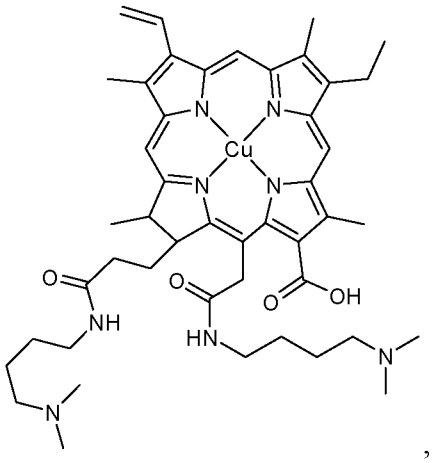
or an agriculturally acceptable salt thereof.

[099] In some implementations, R^1 is H, R^2 is H and/or R^4 is H or alkyl. In some implementations, R^4 is H and R^5 is alkyl. In some implementations, R^4 and R^5 are alkyl. R^4 and/or R^5 can for example be a (C_1-C_{12})alkyl, a (C_1-C_8)alkyl or a (C_1-C_4)alkyl. In some implementations, R^5 is $-(CH_2)_p-NR^9R^{10}$. In some implementations, R^9 and R^{10} are alkyl, or R^9 is H and R^{10} is alkyl. R^9 and/or R^{10} can for example be a (C_1-C_{12})alkyl, a (C_1-C_8)alkyl or a (C_1-C_4)alkyl. In some implementations, n is an integer selected from 1 to 16, or from 1 to 12, or from 1 to 8, or from 1 to 6, or from 1 to 4, or from 2 to 4.

[0100] In some implementations, the compound of Formula I-B2 is:

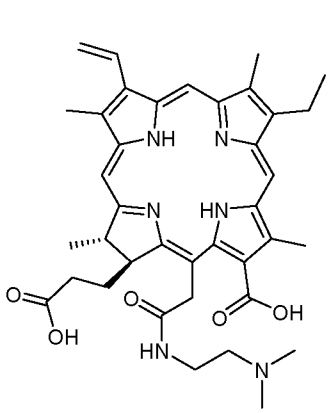
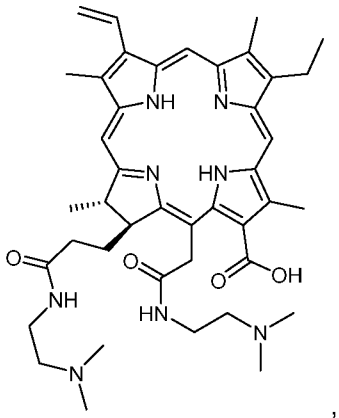

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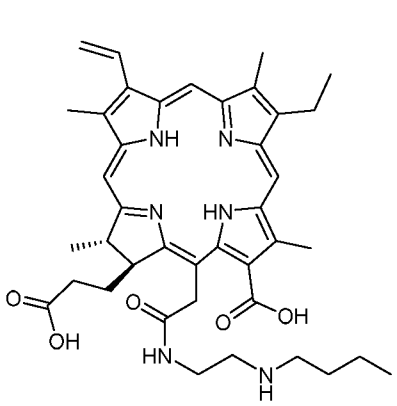









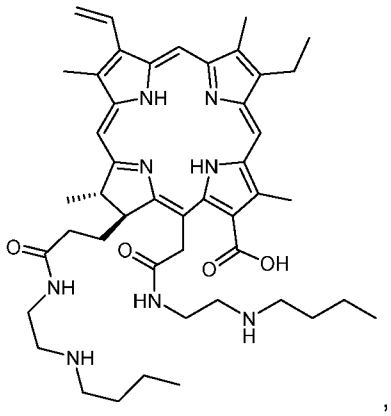
or an agriculturally acceptable salt thereof.

[0101] In some implementations, the compound of Formula I-B2* is:

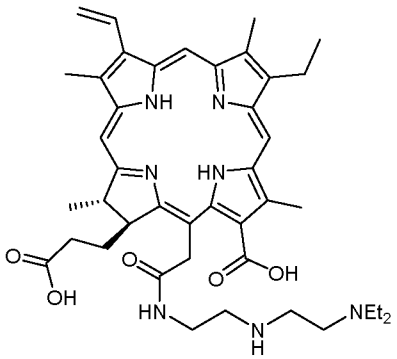





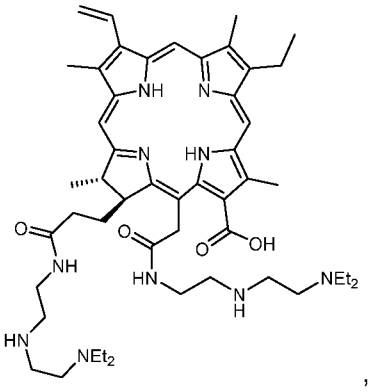
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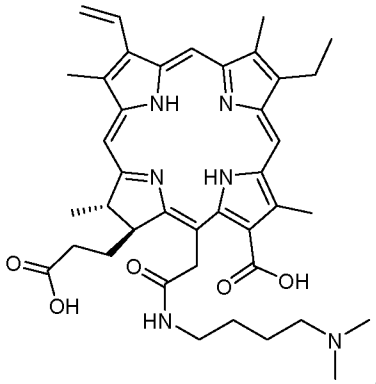
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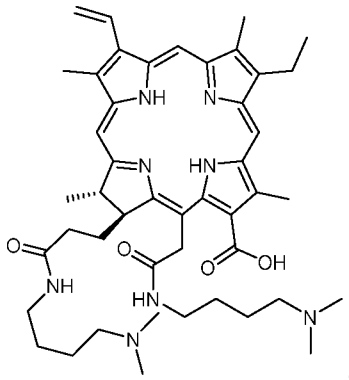
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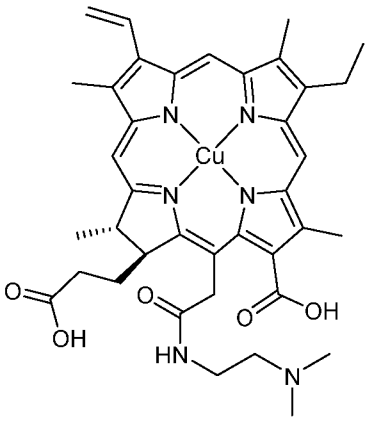
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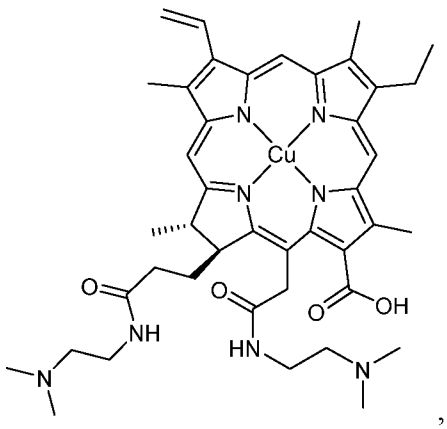
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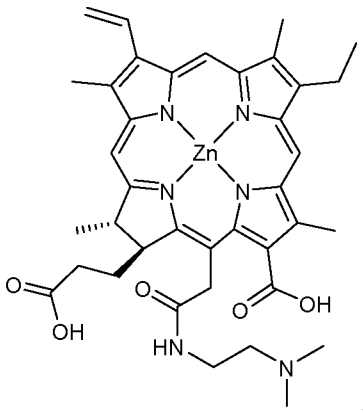
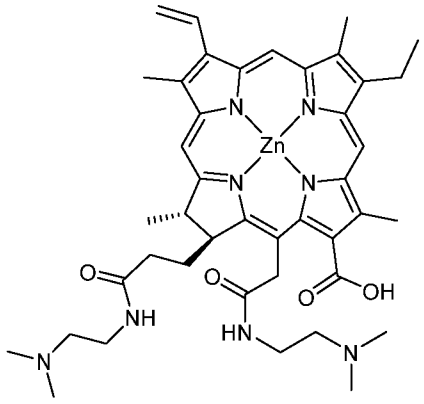
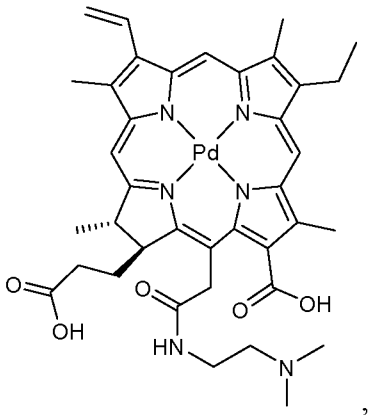
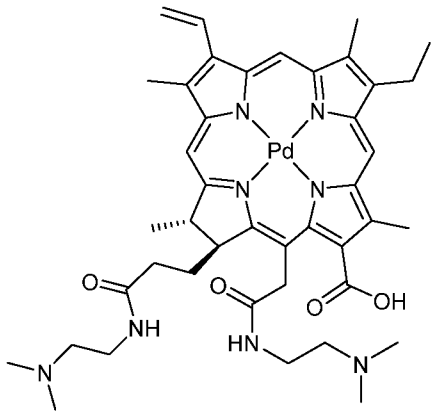
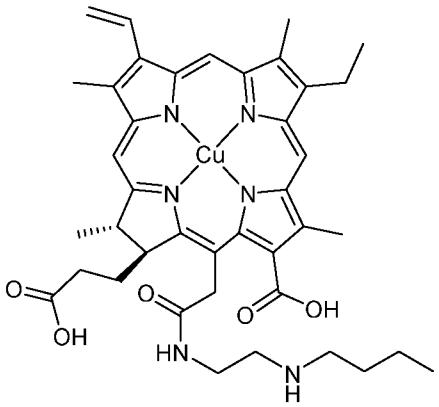
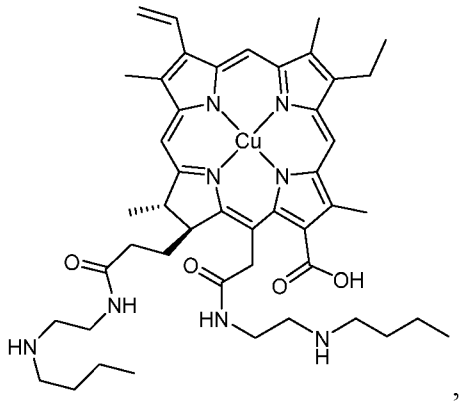
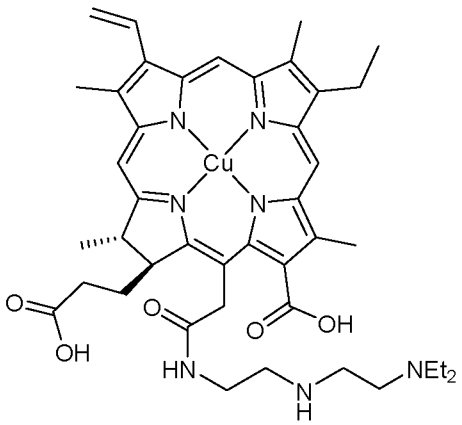
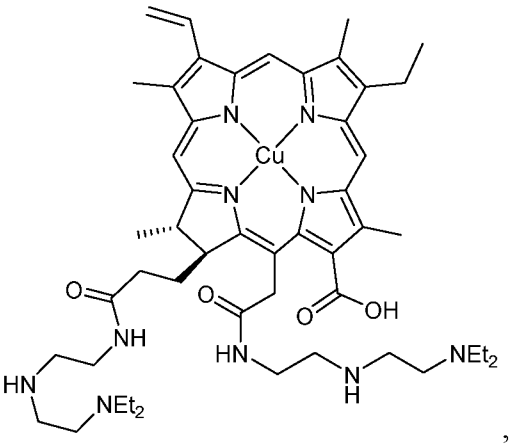
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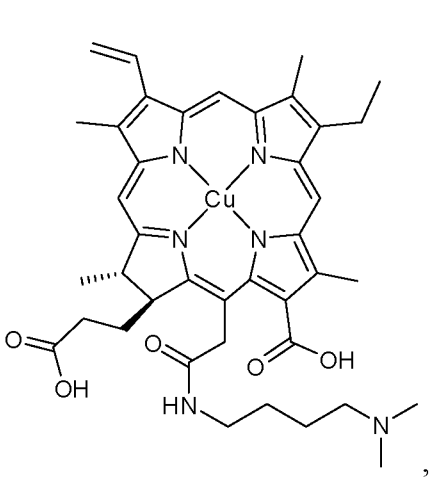


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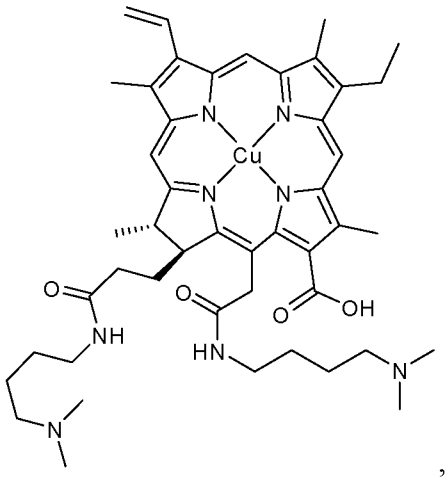


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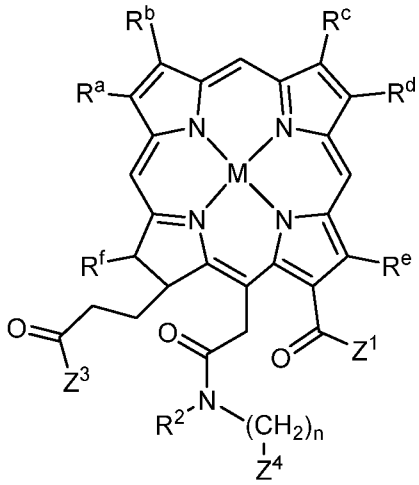
, or



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or an agriculturally acceptable salt thereof.

[0102] In another aspect, there is provided a compound of Formula I-B3:



Formula I-B3

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

Z^4 is $Si(R^7)_3$ or SR^8;

Z^3 is OR^{12} or $Z^3 = NR^2\text{-}(CH_2)_n\text{-}Z^4$;

each R^1, R^2 and R^{12} is, independently, H, alkyl or substituted alkyl;

R^7 is alkyl, O(alkyl) or O(tri-substituted silyl);

R^8 is H, alkyl, substituted alkyl or $-(CH_2CH_2O)_m\text{-}R^{13}$;

R^{13} is H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl, CO(alkyl), CO(substituted alkyl), CO(alkenyl), CO(substituted alkenyl), CO(alkynyl) or CO(substituted alkynyl);

n is an integer selected from 1 to 16;

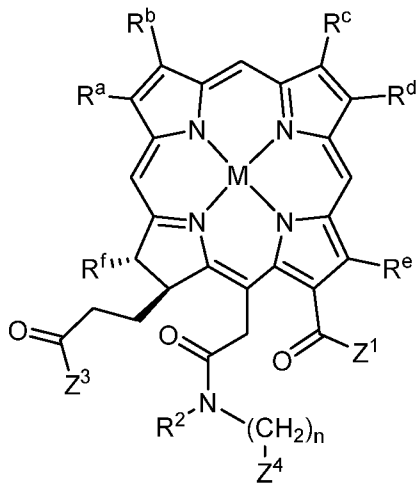
m is an integer selected from 1 to 100;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, CN and N_3.

[0103] In some implementations, the compound of Formula I-B3 is a compound of Formula I-B3*:

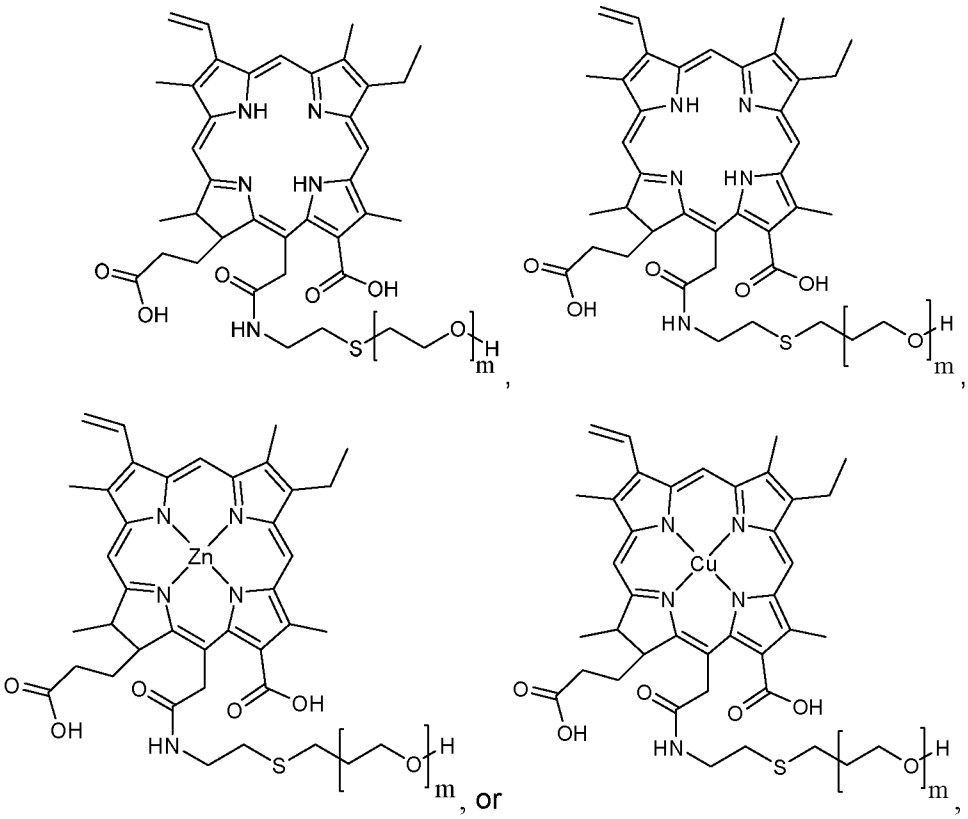


Formula I-B3*

or an agriculturally acceptable salt thereof.

[0104] In some implementations, R^1 is H, R^2 is H and/or R^{12} is H or alkyl. In some implementations, R^7 is alkyl, O(alkyl) or O(tri-substituted silyl), with the alkyl groups being a $(C_1\text{-}C_{12})$alkyl, a $(C_1\text{-}C_8)$alkyl or a $(C_1\text{-}C_4)$alkyl. In some implementations, n is an integer selected from 1 to 16, or from 1 to 12, or from 1 to 8, or from 1 to 6, or from 1 to 4, or from 2 to 4. In some implementations, Z^3 is OR^{12}. In other implementations, $Z^3 = NR^2\text{-}(CH_2)_n\text{-}Z^4$.

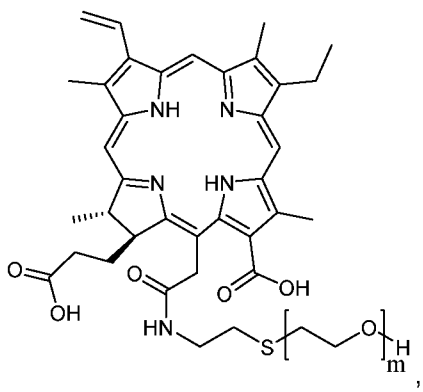
[0105] In some implementations, the compound of Formula I-B3 is



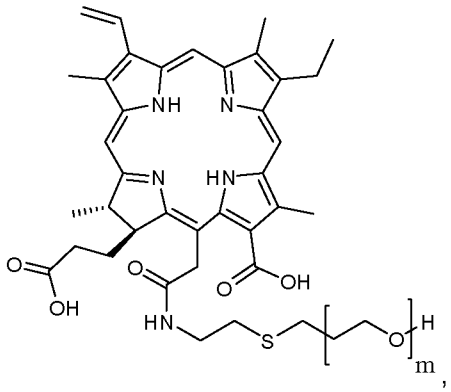
or an agriculturally acceptable salt thereof,

wherein m is an integer selected from 4 to 15.

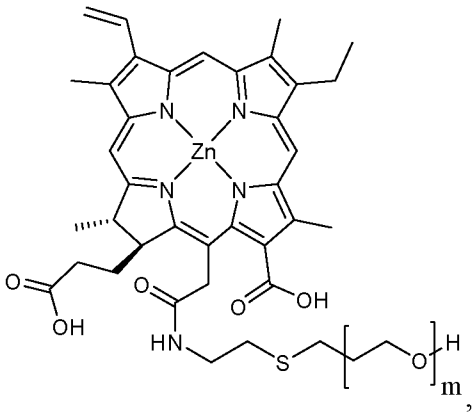
[0106] In some implementations, the compound of Formula I-B3* is



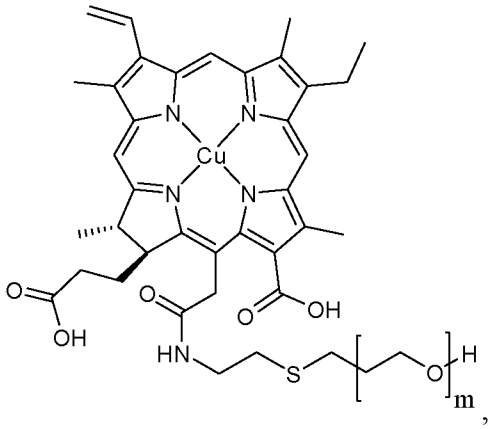
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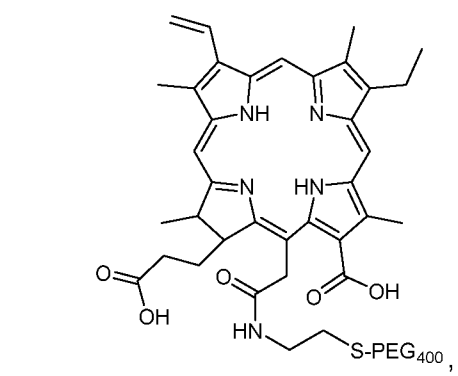


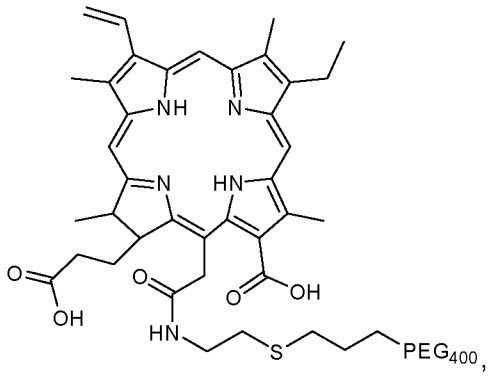
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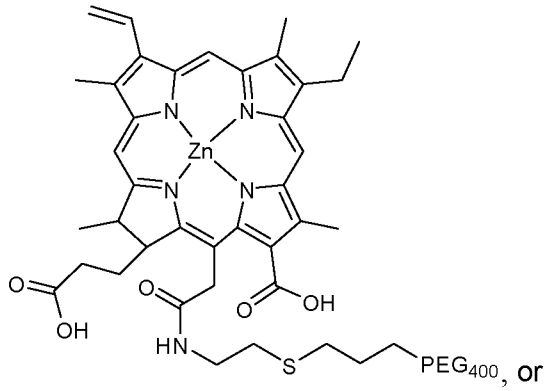
or an agriculturally acceptable salt thereof,

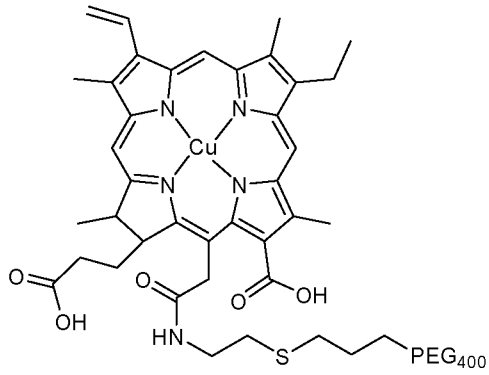
wherein m is an integer selected from 4 to 15.

[0107] In some implementations, the compound of Formula I-B3 is



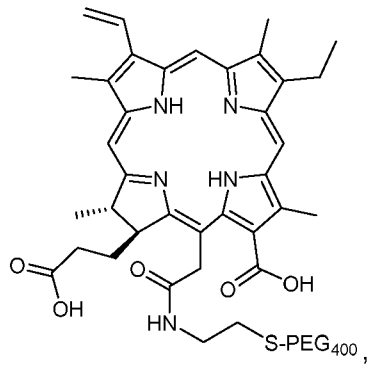


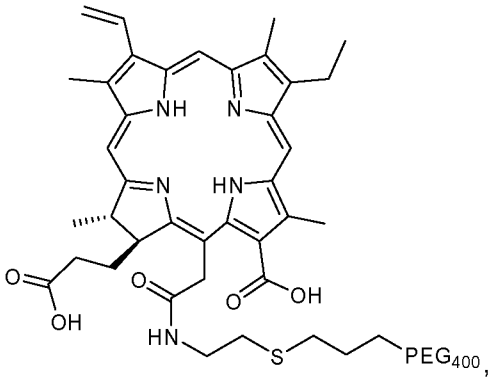


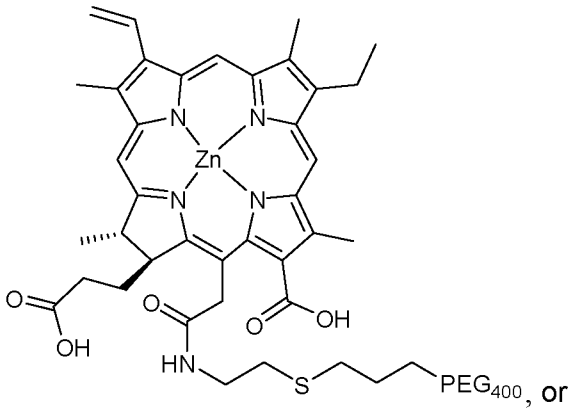


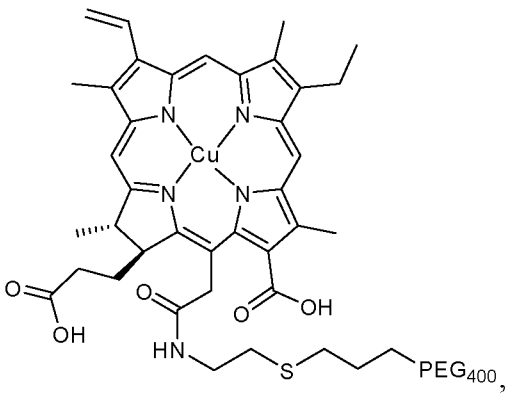
or an agriculturally acceptable salt thereof.

[0108] In some implementations, the compound of Formula I-B3* is



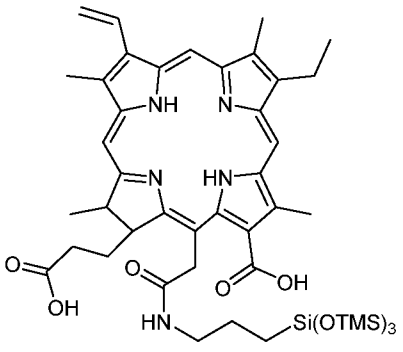




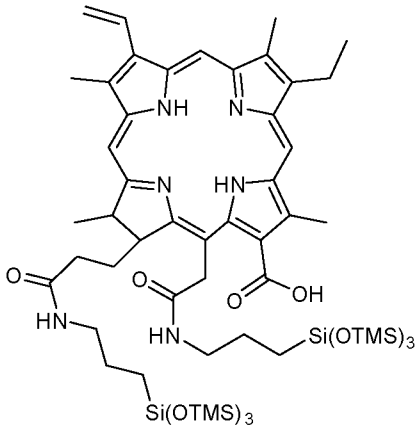


or an agriculturally acceptable salt thereof.

[0109] In some implementations, the compound of Formula I-B3 is:

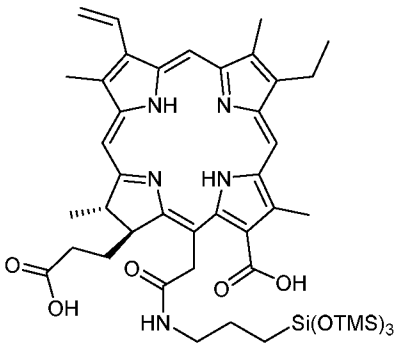


, or

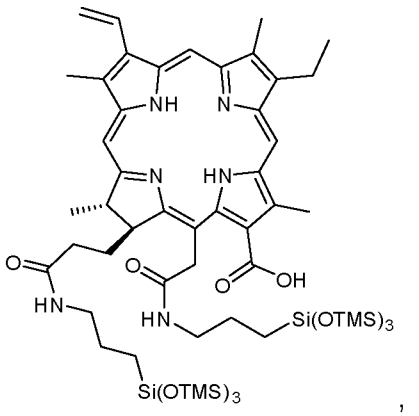


or an agriculturally acceptable salt thereof.

[0110] In some implementations, the compound of Formula I-B3* is



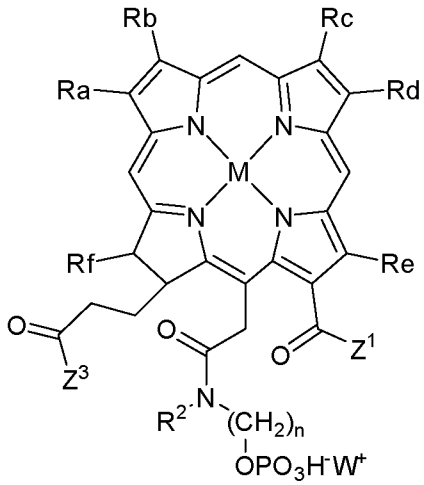
, or



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[0111] or an agriculturally acceptable salt thereof.

[0112] In another aspect, there is provided a compound of Formula I-B4a:



Formula I-B4a

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

Z^3 is OR^{12} or $Z^3 = NR_2\text{-}(CH_2)_n\text{-}O(PO_3H)^- W^+$;

each R^1, R^2 and R^{12} is, independently, H, alkyl or substituted alkyl;

n is an integer selected from 1 to 16;

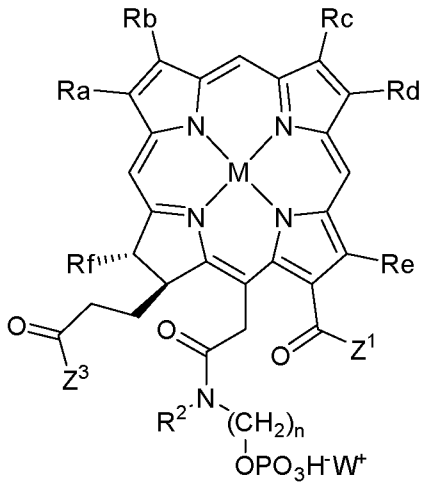
W^+ is an agriculturally acceptable cation;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, CN and N_3.

[0113] In some implementations, the compound of Formula I-B4a is a compound of Formula I-B4a*:

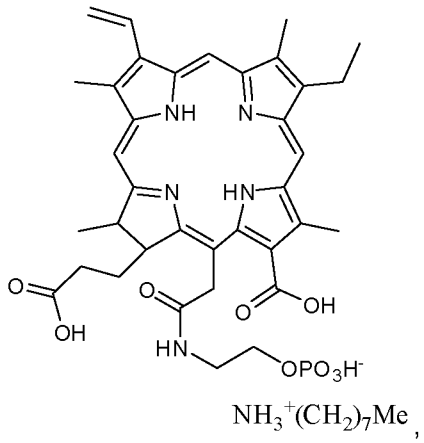


Formula I-B4a*

or an agriculturally acceptable salt thereof.

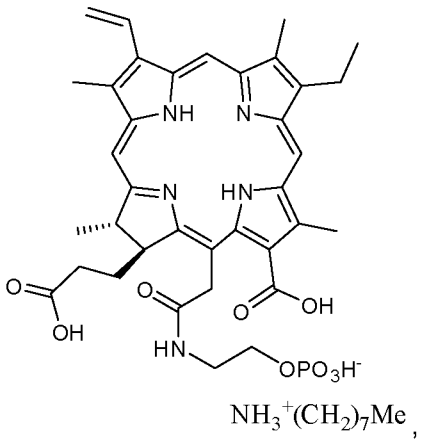
[0114] In some implementations, R^1 is H, R^2 is H and/or R^{12} is H or alkyl. In some implementations, n is an integer selected from 1 to 16, or from 1 to 12, or from 1 to 8, or from 1 to 6, or from 1 to 4, or from 2 to 4. W^+ is selected from the group consisting of sodium, potassium, magnesium and ammonium cations. In some implementations, Z^3 is OR^{12}. In other implementations, $Z^3 = NR_2\text{-}(CH_2)_n\text{-}O(PO_3H)^-W^+$.

[0115] In some implementations, the compound of Formula I-B4a is



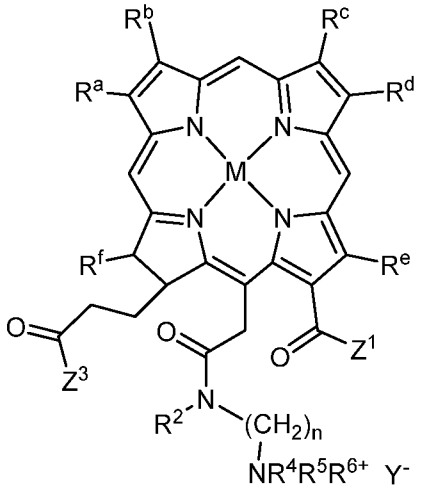
or an agriculturally acceptable salt thereof.

[0116] In some implementations, the compound of Formula I-B4a* is



or an agriculturally acceptable salt thereof.

[0117] In another aspect, there is provided a compound of Formula I-B4c:



Formula I-B4c

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

Z^3 is OR^{12} or $Z^3 = NR_2\text{-}(CH_2)_n\text{-}NR^4R^5R^{6+}\ Y^-$;

each R^1, R^2 and R^{12} is, independently, H, alkyl or substituted alkyl;

each R^4, R^5 and R^6 is, independently, alkyl or substituted alkyl;

n is an integer selected from 1 to 16;

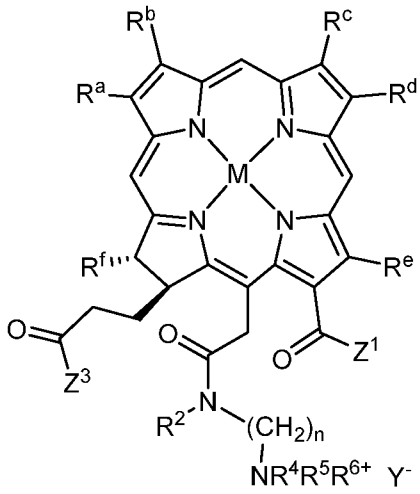
Y^- is an agriculturally acceptable anion;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, CN and N_3.

[0118] In some implementations, the compound of Formula I-B4c is a compound of Formula I-B4c*:

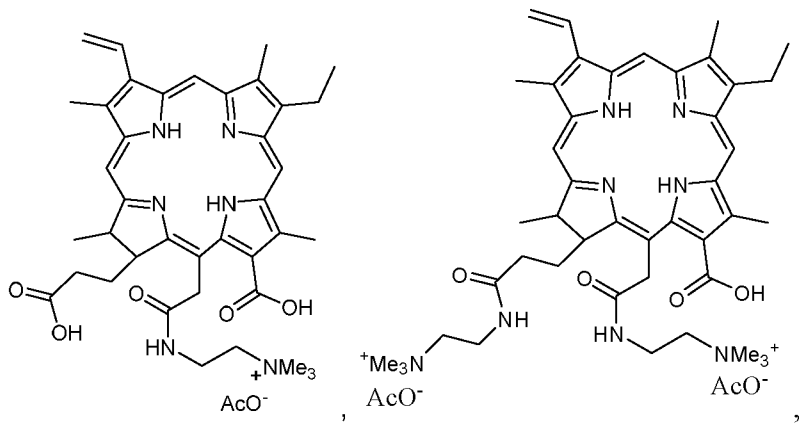


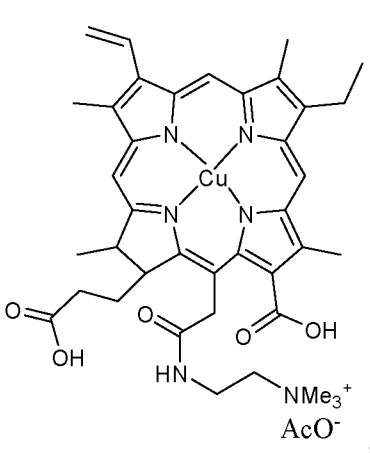
Formula I-B4c*

or an agriculturally acceptable salt thereof.

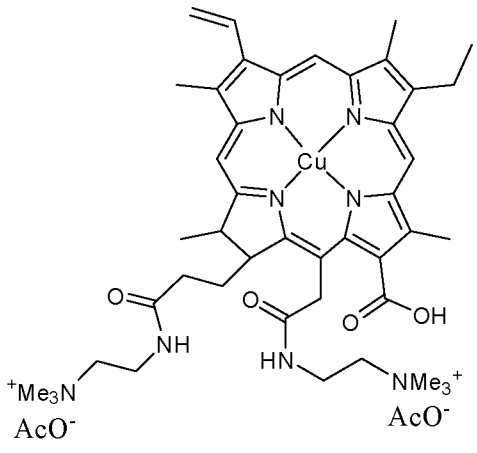
[0119] In some implementations, R^1 is H, R^2 is H and/or R^{12} is H or alkyl. In some implementations, n is an integer selected from 1 to 16, or from 1 to 12, or from 1 to 8, or from 1 to 6, or from 1 to 4, or from 2 to 4. In some implementations, R^4, R^5 and R^6 are alkyl and optionally $R^4 = R^5 = R^6$. Y^- is selected from the group consisting of chloride, bromide, phosphate, dimethylphosphate, methylsulfate, ethylsulfate, acetate and lactate. In some implementations, Z^3 is OR^{12}. In other implementations, $Z^3 = NR_2\text{-}(CH_2)_n\text{-}NR^4R^5R^{6+}\ Y^-$.

[0120] In some implementations, the compound of Formula I-B4c is



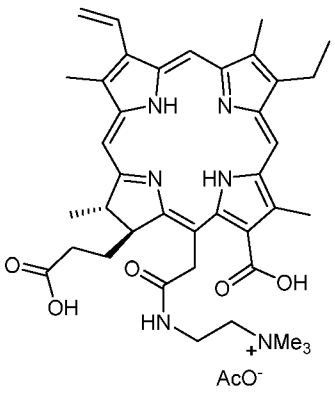


, or

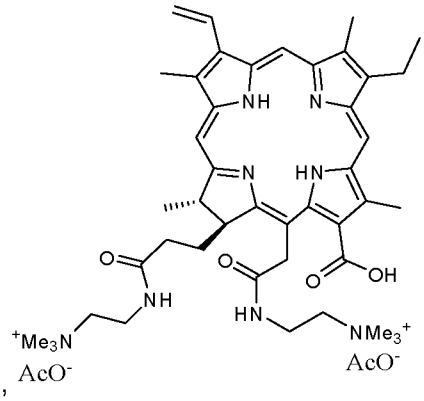


or an agriculturally acceptable salt thereof.

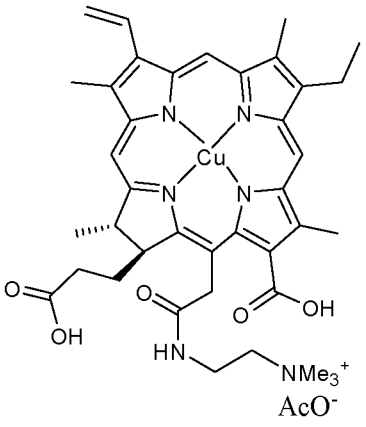
[0121] In some implementations, the compound of Formula I-B4c* is



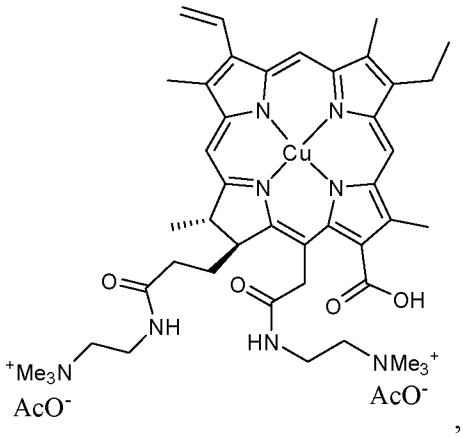
,



,



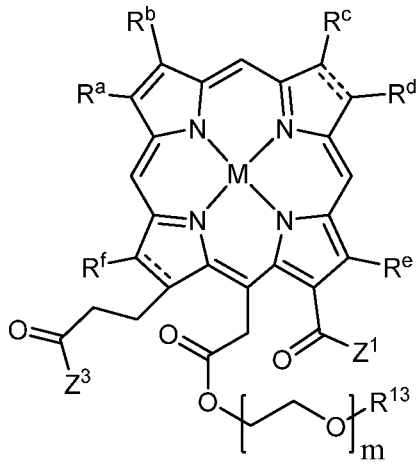
, or



,

or an agriculturally acceptable salt thereof.

[0122] In another aspect, there is provided a compound of Formula I-C:



Formula I-C

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

$Z^3 = OR^{12}$ and m is an integer selected from 1 to 100; or

$Z^3 = O(CH_2CH_2O)_m\text{-}R^{13}$ and m is an integer selected from 5 to 100;

each R^1 and R^{12} is, independently, H, alkyl or substituted alkyl;

R^{13} is H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl, CO(alkyl), CO(substituted alkyl), CO(alkenyl), CO(substituted alkenyl), CO(alkynyl) or CO(substituted alkynyl);

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

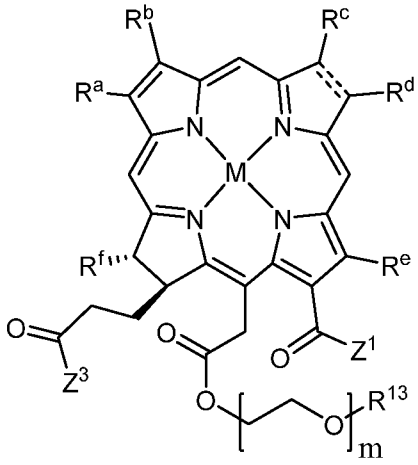
------ is a single bond or a double bond;

------ is a single bond or a double bond; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, CN and N_3.

[0123] In some implementations, the compound of Formula I-C is a compound of Formula I-C*:

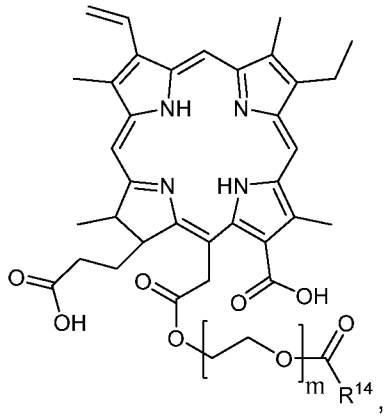


Formula I-C*

or an agriculturally acceptable salt thereof.

[0124] In some implementations, R^1 is H and/or R^{12} is H. In some implementations, m is an integer selected from 5 to 100, or from 5 to 80, or from 5 to 50, or from 5 to 20, or from 5 to 10. In some implementations, Z^3 is OR^{12}. In other implementations, $Z^3 = O(CH_2CH_2O)_m\text{-}R^{13}$. In some implementations, R^{13} is H, alkyl, alkenyl, CO(alkyl) or CO(alkenyl).

[0125] In some implementations, the compound of Formula I-C is:



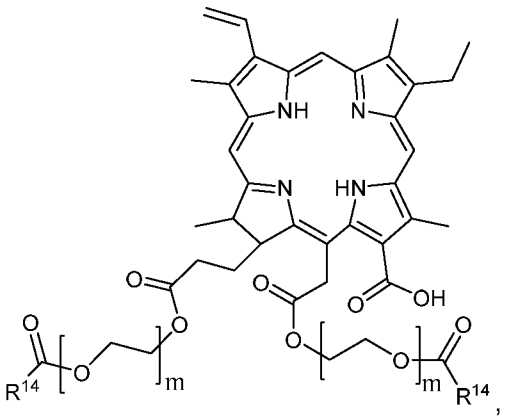
or an agriculturally acceptable salt thereof,

wherein:

m is an integer selected from 1 to 100; and

R^{14} is aryl, alkyl, substituted aryl or substituted alkyl.

[0126] In some implementations, the compound of Formula I-C is:



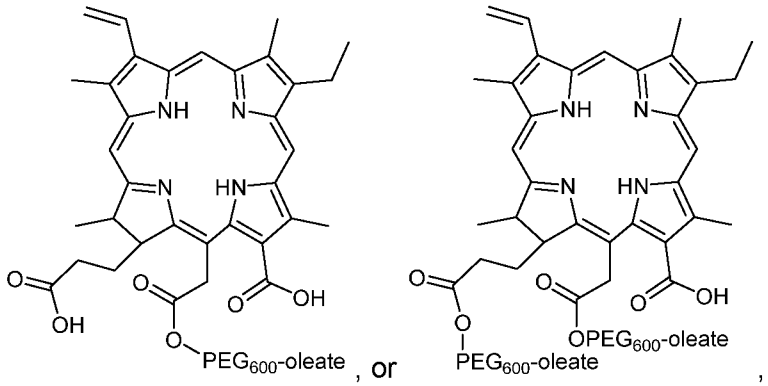
or an agriculturally acceptable salt thereof,

wherein:

m is an integer selected from 5 to 100; and

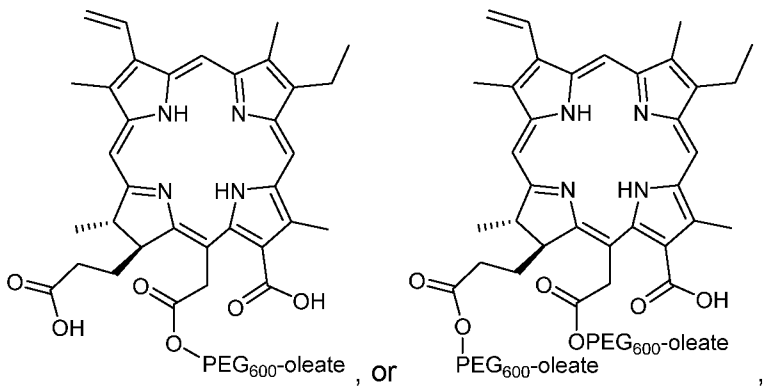
R^{14} is alkyl or substituted alkyl.

[0127] In some implementations, the compound of Formula I-C is:



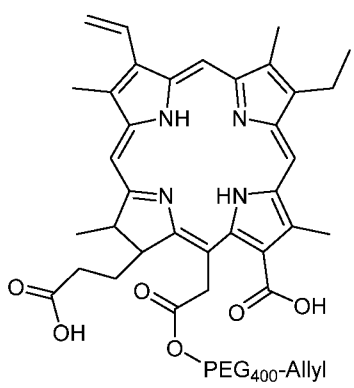
or an agriculturally acceptable salt thereof.

[0128] In some implementations, the compound of Formula I-C* is:

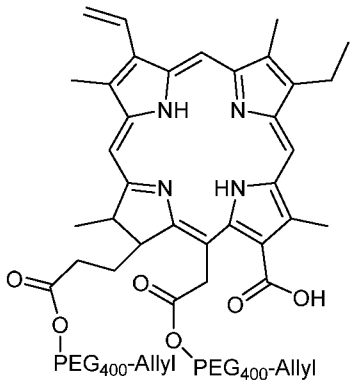


or an agriculturally acceptable salt thereof.

[0129] In some implementations, the compound of Formula I-C is:



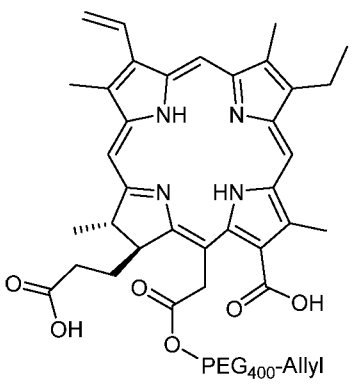
, or



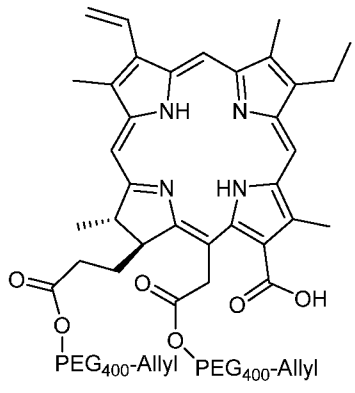
,

or an agriculturally acceptable salt thereof.

[0130] In some implementations, the compound of Formula I-C* is:



, or

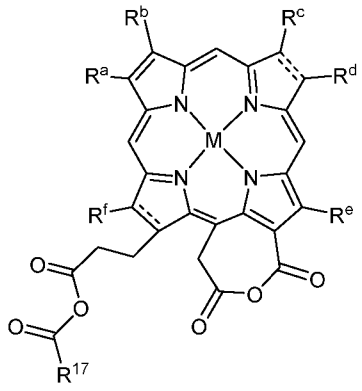


,

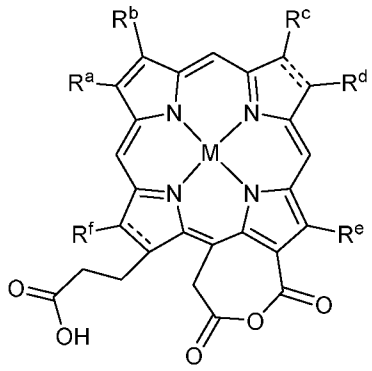
or an agriculturally acceptable salt thereof.

Synthetic intermediates and method of manufacture

[0131] In one aspect, there is provided a compound of Formula II-A and/or Formula II-B, that can be useful in the synthesis of the compounds of Formula I, I-A1, I-B1, I-B2, I-B3, I-B4a, I-B4c and/or I-C described herein:



Formula II-A



Formula II-B

or a salt thereof,

wherein:

R^{17} is H, alkyl, aryl or alkoxy;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

------ is a single bond or a double bond;

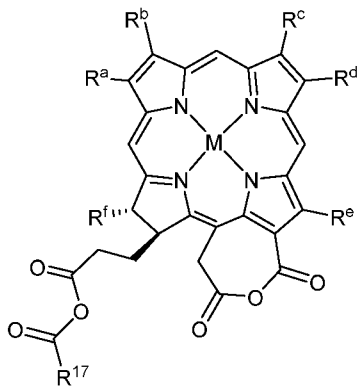
------ is a single bond or a double bond; and

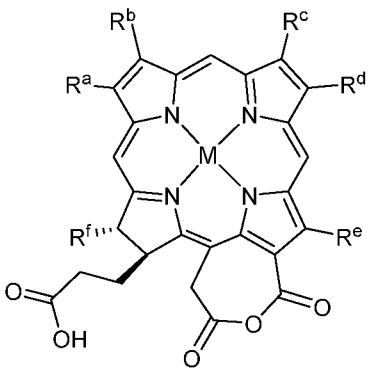
M is 2H or a metal species,

wherein the substituted alkyl, substituted aryl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, alkenyl, CN and N_3.

[0132] In some implementations, ------ is a single bond; and ------ is a double bond.

[0133] In some implementations, the compounds of Formula II-A and Formula II-B is a compound of Formula II-A1* or Formula II-B1*:





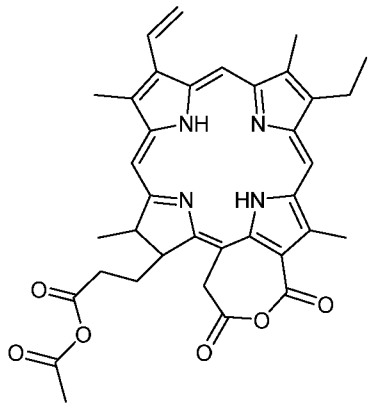
Formula II-A1* Formula II-B1*

or a salt thereof.

[0134] In some implementations, each R^a, R^b, R^c, R^d, R^e and R^f is, independently, alkyl or alkenyl. For example, and without being limiting, R^a, R^c, R^e and R^f can be methyl; R^b can be vinyl; and R^d can be ethyl.

[0135] In some implementations, M is 2H. In other implementations, M is a metal species selected from the group consisting of Mg(II), Zn(II), Pd(II), Sn(IV), Al(III), Pt(II), Si(IV), Ge(IV), Ga(III) and In(III).

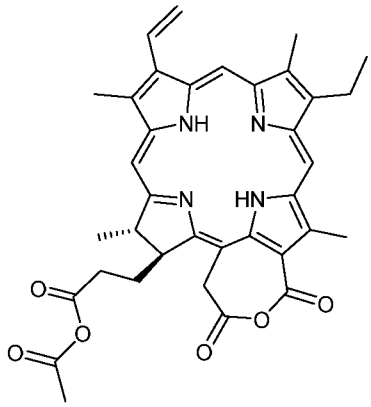
[0136] For example, the compound of Formula II-A can be:



,

or a salt thereof.

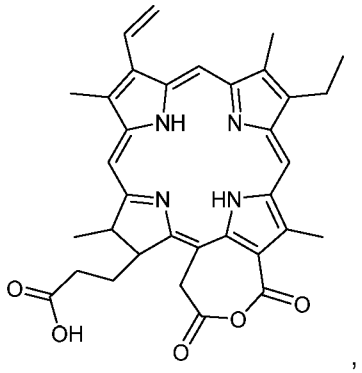
[0137] The compound of Formula II-A1* can be:



,

or a salt thereof.

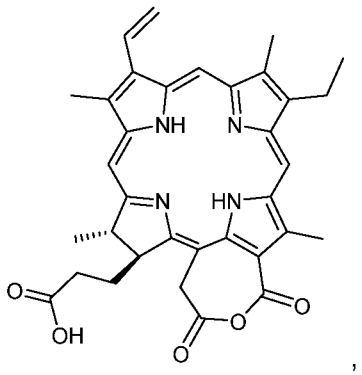
[0138] For example, the compound of Formula II-B can be:



,

or a salt thereof.

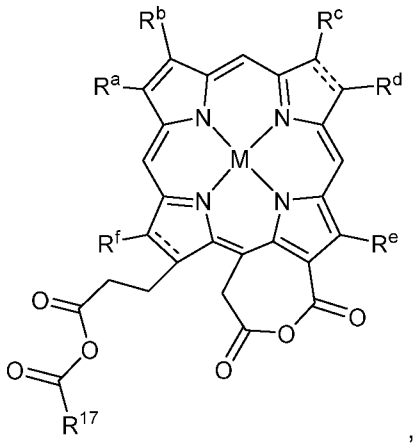
[0139] The compound of Formula II-B1* can be:



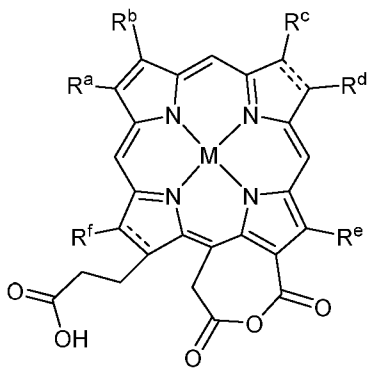
,

or a salt thereof.

[0140] In another aspect, there is provided a method of manufacturing a compound of Formula II-A and/or Formula II-B:



,



Formula II-A Formula II-B

or a salt thereof,

wherein:

R^{17} is H, alkyl, aryl or alkoxy;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

⎓ is a single bond or a double bond;

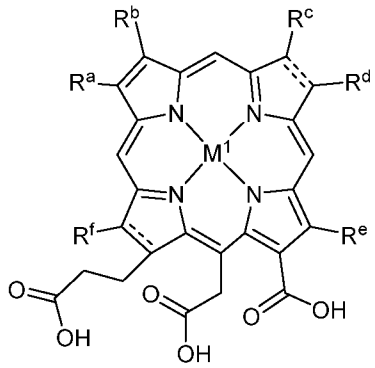
⎓ is a single bond or a double bond; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted aryl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, alkenyl, CN and N_3;

the method comprising:

reacting a compound of Formula III:



Formula III

or a salt thereof, with an anhydride of general formula $(R^{17}CO)_2O$,

M^1 is 2H or a metal species, M^1 being different or the same as M.

[0141] In some implementations, M is 2H and M^1 is 2H. In other implementations M is a metal species and M^1 = M.

[0142] In other implementations, M is a metal species and M^1 is 2H. In such case, the method can further include a metalation reaction of the compound of Formula II-A or Formula II-B wherein M = 2H.

[0143] In other implementations, M is 2H and M^1 is a metal species. In such case, the method can further include a de-metalation reaction of the compound of Formula II-A or Formula II-B, or of the compound of Formula III where M = M^1, to obtain the corresponding compound where M = 2H.

[0144] In other implementations, M^1 is a first metal species and M is a second metal species. In such case, the method can include a trans-metalation reaction to convert the compound of Formula II-A or Formula II-B, or of the compound of Formula III to displace the first metal species and insert the second metal species.

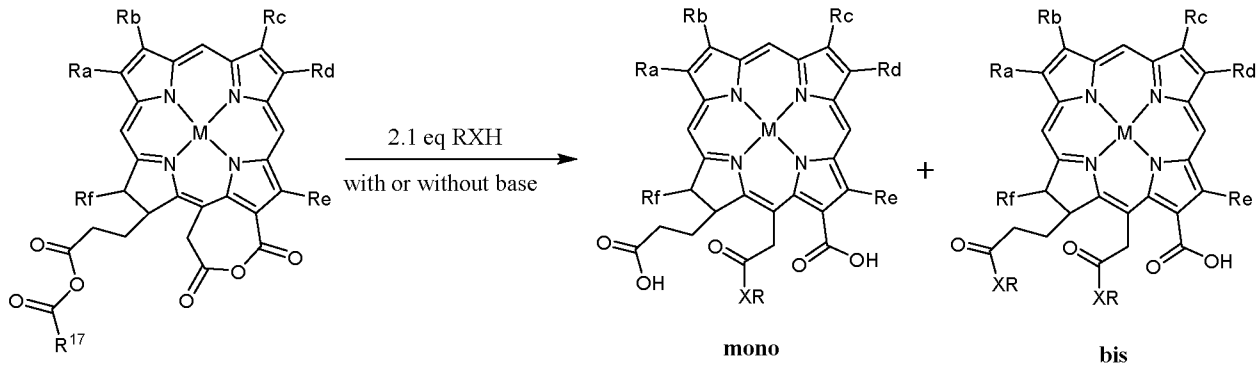
[0145] In some implementations, reacting the compound of Formula III with the anhydride of general formula $(R^{17}CO)_2O$ is performed at a temperature of up to 50°C, or of up to 40°C, or between about 15°C and about 40°C. In some implementations, the temperature is ambient temperature. Reacting the compound of Formula III with the anhydride of general formula $(R^{17}CO)_2O$ can be performed in a solvent. Optionally, the solvent can be $(R^{17}CO)_2O$ (i.e., the reaction can be conducted in "neat" conditions).

[0146] Depending on the identity of the R^{17} group, the molar ratio II-A:II-B can vary. For example, when R^{17} is methyl, the compound of Formula II-A is obtained. In another example, when R^{17} is *tert*-butoxy, the compound of Formula II-B is obtained.

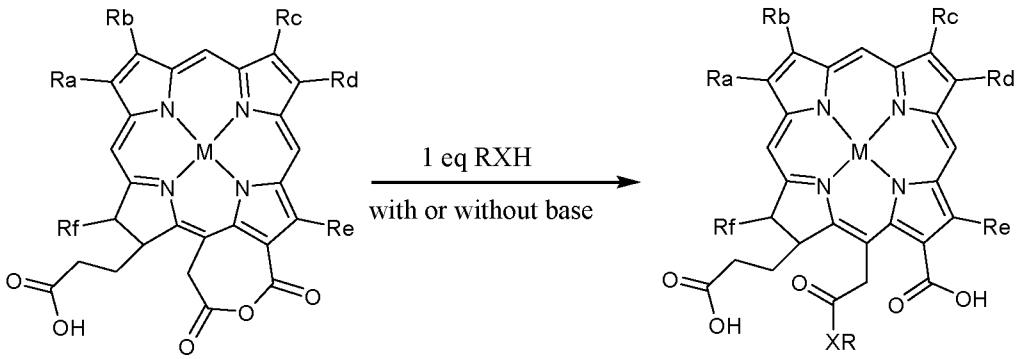
Synthesis of the photosensitizer compounds

[0147] In another, there is provided a method of manufacture of the compounds of Formula I, I-A1, I-B1, I-B2, I-B3, I-B4a, I-B4c and/or I-C described herein, comprising reacting one of the compounds of Formula II-A or Formula II-B, or a salt thereof, with a corresponding nucleophile – e.g., an amine, an alcohol, etc. The reaction can be performed in the presence or in the absence of a base (e.g., sodium bicarbonate).

[0148] For example, a compound of Formula II-A can be reacted with 2 equivalents or more of nucleophile RXH (X = O or X = NH), in the presence or absence of a base, as shown in the scheme below, to give a mixture of mono and bis substituted reaction compounds.



[0149] In another example, a compound of Formula II-B can be reacted with nucleophile RXH (X = O or X = NH), in the presence or absence of a base, as shown in the scheme below, to give the monosubstituted compound.



mono

[0150] Examples of such reactions can be found in the Examples section.

Chelating agent

[0151] In some implementations, the photosensitizer compound can be applied to a plant in combination with a chelating agent (also referred to herein as a permeabilizing agent). In some scenarios, the photosensitizer compound reacts to light by generating ROS, while the chelating agent can increase the overall impact of suppression of the growth of the microbial pathogen, for example by increasing the permeability of the outer membrane of the microbial pathogen to the photosensitizer. It should be understood that the term “chelating agent”, as used herein, refers generally to a compound that can form several chelating bonds to one or several metals or ions.

[0152] In some implementations, the chelating agent can include at least one carboxylic group, at least one hydroxyl group, at least one phenol group and/or at least one amino group or an agriculturally acceptable salt thereof. In some implementations, the chelating agent can include an aminocarboxylic acid compound or an agriculturally acceptable salt thereof. The aminocarboxylic acid or agriculturally acceptable salt thereof can include an amino polycarboxylic acid or an agriculturally acceptable salt thereof. For example, the amino polycarboxylic acid can include two amino groups and two alkylcarboxyl groups bound to each amino group. The alkylcarboxyl groups can be methylcarboxyl groups.

[0153] In some implementations, the chelating agent is selected from the group consisting of: an aminopolycarboxylic acid, an aromatic or aliphatic carboxylic acid, an amino acid, a phosphonic acid, and a hydroxycarboxylic acid or an agriculturally acceptable salt thereof.

[0154] In some implementations, the methods and compositions described herein include one or more aminopolycarboxylic acid chelating agents. Examples of aminopolycarboxylic acid chelating agents include, without limitation, ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethylenediaminetriacetic acid (HEDTA), and ethylenediaminedisuccinate (EDDS), cyclohexanediaminetetraacetic acid (CDTA), N-(2-hydroxyethyl)ethylenediaminetriacetic acid (EDTA-OH) glycol ether diaminetetraacetic acid (GEDTA), alanine diacetic acid (ADA), alkoyl ethylene diamine triacetic acids (e.g., lauroyl ethylene diamine triacetic acids (LED3A)), aspartic acid diacetic acid (ASDA), aspartic acid monoacetic acid, diamino cyclohexane tetraacetic acid (CDTA), 1,2-diaminopropanetetraacetic acid (DPTA-OH), l,3-diamino-2-propanoltetraacetic acid (DTPA), diethylene triamine pentam ethylene phosphonic acid (DTPMP), diglycolic acid, dipicolinic acid (DPA), ethanolamine diacetic acid, ethanol diglycine (EDG), ethylenediaminediglutaric acid (EDDG), ethylenediaminedi(hydroxyphenylacetic acid (EDDHA), ethylenediaminedipropionic acid (EDDP), ethylenediaminedisuccinate (EDDS), ethylenediaminemonosuccinic acid (EDMS), ethylenediaminetetraacetic acid (EDTA), ethylenediaminetetrapropionic acid (EDTP), and ethyleneglycolaminoethylestertetraacetic acid (EGTA) and agriculturally acceptable salts (for example, the sodium salts, calcium salts and/or potassium salts) thereof.

[0155] One non-limiting example of chelating agent is ethylenediaminetetraacetic acid (EDTA) or an agriculturally acceptable salt thereof. The aminocarboxylate salt can for example be a sodium or calcium salt.

[0156] Another non-limiting example of chelating agent is polyaspartic acid or an agriculturally acceptable salt thereof (i.e., a polyaspartate), such as sodium polyaspartate. The molecular weight of the polyaspartate salt can for example be between 2,000 and 3,000.

[0157] The chelating agent can thus be a polymeric compound, which can include aspartate units, carboxylic groups, and other features found in polyaspartates. The polyaspartate can be a co-polymer that has alpha and beta linkages, which may be in various proportions (e.g., 30% alpha, 70% beta, randomly distributed along the polymer chain). One non-limiting example of a sodium polyaspartate is Baypure® DS 100.

[0158] Other non-limiting examples of chelating agents include EDDS (ethylenediamine-N,N'-disuccinic acid), IDS (iminodisuccinic acid (N-1,2-dicarboxyethyl)-D,L-aspartic acid), isopropylamine, triethanolamine, triethylamine, ammonium hydroxide, tetrabutylammonium hydroxide, hexamine, GLDA (L-glutamic acid N,N-diacetic acid), or agriculturally acceptable salts thereof. The chelating agent can be metallated or non-metallated. In some implementations, IDS can be used as a tetrasodium salt of IDS (e.g., tetrasodium iminodisuccinate), which can be Baypure® CX100. In some implementations, EDDS can be used as a trisodium salt of EDDS. In some implementations, GLDA can be used as a tetrasodium salt of GLDA.

[0159] In some implementations, the chelating agent can include one or more amino acid chelating agents. Examples of amino acid chelating agents include, without limitation, alanine, arginine, asparagine, aspartic acid, glutamic acid, glutamine, glycine, histidine, isoleucine, leucine, lysine, methionine, proline, serine, threonine, tyrosine, valine, or salts (for example, the sodium salts, calcium salts and/or potassium salts) and combinations thereof.

[0160] In some implementations, the chelating agent can include one or more aromatic or aliphatic carboxylic acid chelating agents. Examples of aromatic or aliphatic carboxylic acid chelating agents include, without limitation, oxalic acid, succinic acid, pyruvic acid malic, acid, malonic acid, salicylic acid, and anthranilic acid, and salts (for example, the sodium salts, calcium salts and/or potassium salts) thereof. In some implementations, the methods and compositions described herein include one or more polyphenol chelating agents. One non-limiting example of a polyphenol chelating agent is tannins such as tannic acid.

[0161] In some implementations, the chelating agent can include one or more hydroxycarboxylic acid chelating agents. Examples of the hydroxycarboxylic acid type chelating agents include, without limitation, malic acid, citric acid, glycolic acid, heptonic acid, tartaric acid and salts (for example, the sodium salts, calcium salts and/or potassium salts) thereof.

[0162] It will be understood that the one or more chelating agents can be provided as the free acid, as an agriculturally acceptable salt, or as combinations thereof. In some implementations, each of one or more the chelating agent(s) is applied as the free acid. In other implementations, the chelating agent(s) can be applied as a salt. Exemplary salts include sodium salts, potassium salts, calcium salts, ammonium salts, amine salts, amide salts, and combinations thereof. In still other implementations, when more than one chelating

agent is present, at least one of the chelating agents is applied as a free acid, and at least one of the chelating agents is applied as a salt.

Additives and adjuvants

[0163] In some implementations, the photosensitizer compound can be applied to a plant in combination with one or more agriculturally suitable adjuvants. Each of the one or more agriculturally suitable adjuvants can be independently selected from the group consisting of one or more activator adjuvants (e.g., one or more surfactants; e.g., one or more oil adjuvants, e.g., one or more penetrants) and one or more utility adjuvants (e.g., one or more wetting or spreading agents; one or more humectants; one or more emulsifiers; one or more drift control agents; one or more thickening agents; one or more deposition agents; one or more water conditioners; one or more buffers; one or more anti-foaming agents; one or more UV blockers; one or more antioxidants; one or more fertilizers, nutrients, and/or micronutrients; and/or one or more herbicide safeners). Exemplary adjuvants are provided in Hazen, J.L. Weed Technology 14: 773-784 (2000), which is incorporated by reference in its entirety.

[0164] In some implementations, the photosensitizer compound can be applied to a plant in combination with oil. The oil can be selected from the group consisting of a mineral oil (e.g., paraffinic oil), a vegetable oil, an essential oil, and a mixture thereof. In some scenarios, combining the photosensitizer compound with an oil can improve solubility of the photosensitizer compound when in contact with the plant. The oil can be added with the photosensitizer compound, or separately, in the presence or absence of a carrier fluid such as water.

[0165] Non-limiting examples of vegetable oils include oils that contain medium chain triglycerides (MCT), or oil extracted from nuts. Other non-limiting examples of vegetable oils include coconut oil, canola oil, soybean oil, rapeseed oil, sunflower oil, safflower oil, peanut oil, cottonseed oil, palm oil, rice bran oil or mixtures thereof. Non-limiting examples of mineral oils include paraffinic oils, branched paraffinic oils, naphthenic oils, aromatic oils or mixtures thereof.

[0166] Non-limiting examples of paraffinic oils include various grades of poly-alpha-olefin (PAO). For example, the paraffinic oil can include HT60™, HT100™, High Flash Jet, LSRD™, and N65DW™. The paraffinic oil can include a paraffin having a number of carbon atoms ranging from about 12 to about 50, or from about 16 to 35. In some scenarios, the paraffin

can have an average number of carbon atoms of 23. In some implementations, the oil can have a paraffin content of at least 80 wt%, or at least 90 wt%, or at least 99 wt%.

[0167] The photosensitizer compound and the oil can be added sequentially or simultaneously. When added simultaneously, the nitrogen-bearing macrocyclic compound and the oil can be added as part of the same composition or as part of two separate compositions. In some implementations, the nitrogen-bearing macrocyclic compound and the oil can be combined in an oil-in-water emulsion. That is, the combination can include the nitrogen-bearing macrocyclic compound combined with the oil and water so that the combination is formulated as an oil-in-water emulsion. The oil-in-water emulsion can also include other additives such as a chelating agent, a surfactant or combinations thereof.

[0168] As used herein, the term "oil-in-water emulsion" refers to a mixture in which one of the oil (e.g., the paraffinic oil) and water is dispersed as droplets in the other (e.g., the water). In some implementations, an oil-in-water emulsion is prepared by a process that includes combining the paraffinic oil, water, and any other components and the paraffinic oil and applying shear until the emulsion is obtained. In other implementations, an oil-in-water emulsion is prepared by a process that includes combining the paraffinic oil, water, and any other components in the mixing tank and spraying through the nozzle of a spray gun.

[0169] In some implementations, the photosensitizer compound is part of a composition that includes a carrier fluid. A suitable carrier fluid can allow obtaining a stable solution, suspension and/or emulsion of the components of the composition in the carrier fluid. In some implementations, the carrier fluid is water. In other implementations, the carrier fluid is a mixture of water and other solvents or oils that are non-miscible or only partially soluble in water.

[0170] In some implementations, a combination of photosensitizer compound and oil can be used to inhibit growth of a microbial pathogen in a plant. The combination can be an oil-in-water emulsion, where the surfactant is selected such that the photosensitizer compound is maintained in dispersion in the oil-in-water emulsion for delivery to the plant.

[0171] The combination can include a surfactant (also referred to as an emulsifier). The surfactant can be selected from the group consisting of an ethoxylated alcohol, a polymeric surfactant, a fatty acid ester, a poly(ethylene glycol), an ethoxylated alkyl alcohol, a monoglyceride, an alkyl monoglyceride, an amphipathic glycoside, and a mixture thereof. For

example, the fatty acid ester can be a sorbitan fatty acid ester. The surfactant can include a plant derived glycoside such as a saponin. The surfactant can be present as an adjuvant to aid coverage of plant foliage. The surfactant can be an acceptable polysorbate type surfactant (e.g., Tween 80), a nonionic surfactant blend (e.g., Altox™ 3273), or another suitable surfactant.

[0172] In some implementations, the poly(ethylene glycol) can include a poly(ethylene glycol) of Formula R^{15}-O-$(CH_2CH_2O)_f$-R^{16}, wherein: each R^{15} and R^{16} is each, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, CO(alkyl) or CO(substituted alkyl); and f is an integer selected from 1 to 100; wherein the substituted alkyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, alkenyl, CN and N_3.

Compositions including a photosensitizer compound

[0173] It should also be understood that the photosensitizer compounds and the other agents (e.g., chelating agent, oil, surfactant, etc.) can be provided to a plant separately or together as part of the same composition. In some implementations, the components of the compositions can be packaged in a concentrated form, without carrier fluid, and the carrier fluid (e.g., water) can be added to form the composition directly by the operator that can then apply the composition to plants.

[0174] When the components are provided as part of a single composition, the composition can be provided to have certain concentrations and relative proportions of components. For example, the composition can have between about 100 nM and about 50 mM, between about 5 micromolar and about 10 mM, between about 1 micromolar and about 1000 micromolar, between about 5 micromolar and about 200 micromolar of the photosensitizer compound, between about 10 micromolar and about 150 micromolar of the nitrogen-bearing macrocyclic compound, between about 25 micromolar and about 100 micromolar of the nitrogen-bearing macrocyclic compound, or between about 50 micromolar and about 75 micromolar of the photosensitizer compound.

[0175] For example, and without being limiting, the composition can also include between about 2 micromolar and about 10,000 micromolar of the chelating agent, between about 5 micromolar and about 5,000 micromolar of the chelating agent, between about 10 micromolar and about 1,000 micromolar of the chelating agent, between about 25 micromolar and about

500 micromolar of the chelating agent, or between about 50 micromolar and about 100 micromolar of the chelating agent.

[0176] For example, and without being limiting, the relative proportion, by weight, of the nitrogen-bearing macrocyclic compound and the chelating agent in the composition can be between about 50:1 and about 1:1000, between about 20:1 and about 1:500, between about 10:1 and about 1:100, or between about 1:1 and about 1:10.

[0177] For example, and without being limiting, the photosensitizer compound and the oil can be applied in a relative proportion, by weight, between about 50:1 and about 1:1000, between about 20:1 and about 1:500, between about 10:1 and about 1:100, or between about 1:1 and about 1:10.

[0178] The composition including the photosensitizer compound can be applied to plants in various ways. For example, the composition can be prepared to include the photosensitizer compound, a chelating agent as well as a delivery fluid, such as water or a water-oil emulsion. The composition can be applied to the plant by spraying, misting, sprinkling, pouring, or any other suitable method. The anti-microbial composition can be applied to the foliage, roots and/or stem of the plant. Other additives can also be included in the anti-microbial composition, and other application methods can also be performed.

[0179] The plants on which the composition is applied can be outdoors or indoors (e.g., greenhouse) where they are exposed to natural sunlight, or in an indoor location where they are exposed to artificial light. The exposure to the incident light is provided such that the photosensitizer compound can generate ROS that, in turn, facilitate disruption of microbial growth.

[0180] In some implementations, the photosensitizer compound can be used to treat seeds or seedlings. In some scenarios, the treatment of seeds or seedlings can stimulate germination and growth, and/or can increase resistance of the plant to abiotic stresses. In some implementations, the seeds or seedlings can be treated with the photosensitizer compound prior to being planted into a growing medium. In some implementations, the seeds or seedlings can be treated with the photosensitizer compound after being planted into a growing medium.

[0181] The photosensitizer compound can be directly surface-coated onto the seeds, applied to seedlings roots or seedlings leafs (foliar application on seedlings). In some

implementations, a solution or emulsion containing the photosensitizer compound can be directly sprayed onto the seeds or seedlings. In some implementations, the seeds or seedlings can be dipped into a solution or emulsion containing the photosensitizer compound. In some implementations, the root of the seedling can be dipped into a solution or emulsion containing the photosensitizer compound. In some implementations, the seeds can be placed into a container, and a solution containing the photosensitizer compound can be introduced into the container. The container can then be shaken for an appropriate period (e.g., between about 1 minute to several minutes) such that the solution contacts the seeds. The shaken seeds can then be dried (e.g., air dried) prior to being planted.

[0182] The photosensitizer compound can be applied once, twice, or more than twice to seeds or seedlings, using various modes of application. For example, the seeds can be treated after having been planted into a growing medium. In another example, the seeds and/or seedlings can be treated prior to having been planted and after having been planted (e.g., in furrow treatment and/or foliar application). In yet another example, the seed can be treated prior to having been planted and/or after having been planted, and the ensuing seedling can be further treated (e.g., root treatment and/or foliar treatment).

Microbial pathogens

[0183] The microbial pathogens to which the composition including the photosensitizer compound can be applied include fungal and bacterial pathogens. In such case, the composition can be referred to as an “anti-microbial composition”.

[0184] The fungal pathogens to which the anti-microbial composition can be applied include *Alternaria solani*, which can infect plants such as tomatoes and potatoes; *Botrytis cinerea*, which can infect grapes, as well as soft fruits and bulb crops; or *Sclerotinia homoeocarpa*, which can commonly infect turfgrasses. Other fungal pathogens in the *Alternaria, Botrytis* or *Sclerotinia* genera can also receive application of the anti-microbial composition. The anti-microbial composition can be applied to plants that are affected or susceptible to pathogens that cause various plant diseases, e.g., *Colletotrichum*, *Fusarium*, *Puccinia*, *Erysiphaceae, Cercospora, Rhizoctonia, Bipolaris, Microdochium, Venturia inaequalis, Monilinia fructicola, Gymnosporangium juniperi-virginianae, Plasmodiophora brassicae, Ustilago zeae, Phytophthora, Pythium, Fusarium oxysporum, Phytophthora infestans, Taphrina deformans, Powdery Mildew, Phragmidium spp.,* or other fungal pathogens.

[0185] The bacterial pathogens to which the anti-microbial composition can be applied include gram-negative bacteria, such as *Erwinia amylovara*, or other bacterial pathogens in the genus *Erwinia* that can infect woody plants. *E. amylovara* causes fire blight on various plants, including pears, apples, and other *Rosaceae* crops. The anti-microbial composition can be applied to plants that are affected or susceptible to pathogens that cause various plant diseases, e.g., *Pseudomonas, Xanthomonas, Agrobacterium, Curtobacterium, Streptomyces, E. Coli, Xylella fastidiosa* (which causes Olive Quick Decline Syndrome (OQDS) disease), or other bacterial pathogens.

[0186] It is also noted that the anti-microbial compositions described herein can have various inhibitory effects on the microbial pathogens depending on the type of plant and pathogen as well as the state of microbial infection. While herein it is described that the anti-microbial composition can inhibit microbial pathogen growth on a plant, such expressions should not be limiting but should be understood to include suppression of microbial pathogens, prevention against microbial pathogens, killing of microbial pathogens or generally increase toxicity toward microbial pathogens.

Abiotic stresses

[0187] As mentioned above, in some implementations, the photosensitizer compounds and compositions of the present description can be used to increase tolerance of plants to one or more abiotic stresses such as photooxidative conditions, drought (water deficit), excessive watering (flooding, and submergence), extreme temperatures (chilling, freezing and heat), extreme levels of light (high and low), radiation (UV-B and UV-A), salinity due to excessive Na^+ (sodicity), chemical factors (e.g., pH), mineral (metal and metalloid) toxicity, deficiency or excess of essential nutrients, gaseous pollutants (ozone, sulfur dioxide), wind, mechanical factors, and other stressors.

Cold hardiness

[0188] When the abiotic stress is cold stress, application of the photosensitizer compound, alone or in combination with additives such as an oil, a surfactant and/or a chelating agent, can improve cold hardiness of the plant. That is, application of the photosensitizer compound can allow the plant to withstand temperature conditions that are colder than would typically be experienced in the plant's optimal or native growing conditions. Various types of cold stress are possible, such as unexpected frost (for example an early fall frost when healthy

crop, fruit, grain, seeds or leaves are still present on the plant, or a late spring frost that occurs after spring plant growth has begun), a cooler than average growing season, colder than native winter conditions, minimal winter snow cover, ice accumulation, etc.

[0189] It should be noted that what constitutes a cold stress condition for one plant may not be a cold stress condition for another plant. With reference to the USDA zone map, a cold stress condition for a zone 9 plant may in fact be a native growing condition for a zone 8 plant. Likewise, the depth of snow cover required for survival of one type of plant may not be required for a second type of plant. It is therefore understood that various types of cold stress are possible, depending on the type of plant in question.

[0190] The photosensitizer compound, compositions or combinations described herein may be used to protect plants, including woody plants, non-woody plants and turfgrasses, from frost injury. The frost can be an early frost, for example before harvest, after harvest and before dormancy. The frost can be a late frost, for example after budding. The cold damage can also be winter kill induced by winter temperatures, which may result in a loss of viable branches or shoots and lead to plant mortality. Plants treated by the photosensitizer compound, compositions or combinations described herein can be frost or cold sensitive plants, in that they are naturally susceptible to frost, freezing or cold damage or injury in economically or aesthetically significant amounts.

[0191] Increasing resistance to cold stress can be exemplified by a delayed onset of dormancy. Plant dormancy can be triggered by a drop in temperature, e.g., the onset of cold stress. By increasing resistance of the plant to cold stress, dormancy of the plant can be delayed until triggered by a further drop in temperature.

[0192] The photosensitizer compound, compositions or combinations described herein can be used periodically (e.g., at 2 or 3-week intervals starting with spring at breaking the dormancy) and/or by applying one or more treatments (e.g., 2 in the fall), to provide a response in reducing or delaying the dormancy period of certain plants.

[0193] As used herein, the term “reducing dormancy period” refers to a plant that has a reduced dormancy period or extended growing period relative to a control, e.g., a non-treated plant.

[0194] In some implementations, the harvesting step may be carried out one week, one month, two months or more after the last application of the photosensitizer compound,

compositions or combinations described herein, with the active agent still being effective to reduce the effects of cold stress on the plant during the intervening period.

[0195] In some scenarios, resistance to cold stress includes resistance to early or late frost, or winter damage. In some scenarios, the photosensitizer compound, compositions or combinations described herein can be used to protect early growth from cold during fluctuations in temperature (e.g., in early spring). In some scenarios, the photosensitizer compound, compositions or combinations described herein can be used to protect plants from cold during the cold months (e.g., in winter).

[0196] In some scenarios, the photosensitizer compound, compositions or combinations described herein can be applied by soil drenching and/or foliar application (e.g., sprayed until run-off) at the onset or prior to exposure to the low temperature (e.g., fall when the trees have full healthy and vigorous foliage). In some scenarios, the photosensitizer compound, compositions or combinations described herein can be applied by soil drenching and/or foliar application (e.g., sprayed until run-off) during late fall and winter (e.g., for warm climates). In some scenarios, the photosensitizer compound, compositions or combinations described herein can be applied by soil drenching in the late fall following by a foliar application (e.g., sprayed until run-off) in the winter in order to reach maximum hardiness.

[0197] In some scenarios, the photosensitizer compound, compositions or combinations described herein can be applied 1-4 times at a 1 to 6-month interval (e.g., every 2 to 3 months). Further treatments may be applied in the spring and/or during the growing season to improve resistance to subsequent cold stress conditions.

Heat hardiness

[0198] When the abiotic stress is heat stress, application of the photosensitizer compound, compositions or combinations described herein can improve tolerance to high temperatures during the growing season. That is, application of the photosensitizer compound, compositions or combinations described herein can allow the plant to withstand temperature conditions that are higher than would typically be experienced in the plant's optimal or native growing conditions. Heat stress can have various causes, such as lack of shade for plants that typically require shaded growing conditions, or higher than normal soil and air temperatures.

[0199] It should be noted that what constitutes a heat stress condition for one plant may not be a heat stress condition for another plant.

Photooxidative hardiness

[0200] When the abiotic stress is photooxidative stress, application of the photosensitizer compound, compositions or combinations described herein can improve tolerance to stressful light condition during periods of increased generation of reactive oxygen species. That is, application of the photosensitizer compound, compositions or combinations described herein can allow the plant to withstand light exposure conditions (e.g., ultraviolet irradiation conditions) that are higher than would typically be experienced in the plant's optimal or native growing conditions. Photooxidative stress can have various causes, such as high light conditions or certain types of lighting that induce formation of free radicals.

[0201] It should be noted that what constitutes a photooxidative stress condition for one plant may not be a photooxidative stress condition for another plant.

Shade hardiness

[0202] Shade stress, or "low light (LL) stress" can be a problem that influences plant growth and quality. When the abiotic stress is shade stress, application of the photosensitizer compound, compositions or combinations described herein can improve shade hardiness of the plant. That is, application of the photosensitizer compound, compositions or combinations described herein can allow the plant to withstand shady conditions for plants whose optimal or native growing conditions typically require partial or full sun exposure. Various types of shade stress are possible, such as a prolonged period of cloudy weather, excessive growth of adjacent plants or trees that cast shade onto the plant, or lack of availability of a sunny planting location.

[0203] Shade can be a periodic problem. For example, during certain months of the year, a structure situated near a plant may cast a shadow on the plant, causing a shade stress. As the earth moves over the course of a year, the structure may no longer cast the shadow on the plant for another series of months and then the situation can be repeated during the next annual cycle. In such instances, the photosensitizer compound, compositions or combinations described herein can be applied to the plant prior to onset of the period of shade stress and can also be applied during the period of shade stress. The damage to the plant

that would typically result on account of the period of shade stress can be prevented or reduced.

[0204] Shade conditions are not considered to be an abiotic stress condition for many types of plants, as some plants have a requirement for shade as part of their optimal growing conditions. It should also be noted that what constitutes a shade stress condition for one plant may not be a shade stress condition for another plant.

Drought hardiness

[0205] Drought can be defined as the absence of rainfall or irrigation for a period of time sufficient to deplete soil moisture and injure plants. Drought stress results when water loss from the plant exceeds the ability of the plant's roots to absorb water and/or when the plant's water content is reduced enough to interfere with normal plant processes. The severity of the effect of a drought condition may vary between plants, as the plant's need for water may vary by plant type, plant phenological stage, plant age, root depth, soil quality, etc.

[0206] The photosensitizer compound, compositions or combinations described herein can be applied to a plant prior to onset of a drought and/or during a drought. Application of the photosensitizer compound, compositions or combinations described herein can increase the resistance of the plant to the drought stress. Increasing resistance can include maintaining or increasing a quality of the plant as compared to an untreated plant subjected to the same drought stress. Increasing resistance can include reducing the degradation in quality of the plant, as compared to an untreated plant subjected to the same drought stress. If plants do not receive adequate rainfall or irrigation, the resulting drought stress can reduce growth more than all other environmental stresses combined.

[0207] It should also be noted that what constitutes a drought stress condition for one plant may not be a drought stress condition for another plant.

Prevention of salt damage

[0208] Salts can be naturally present in the growing environment of a plant. Salinity stress refers to osmotic forces exerted on a plant when the plant is growing in a saline soil or under other excessively saline conditions. For example, plants growing near a body of salt water can be exposed to salt present in the air or in water used to water the plants. In another example, salt applied to road, sidewalk and driveway surfaces during the winter for improved

driving conditions can be transferred and/or leach into the soil of plants growing in the proximity. Such increased salt content in a growing environment of the plant can result in salinity stress, which can damage the plant.

[0209] Application of the photosensitizer compound, compositions or combinations described herein to the plant can increase the plant's resistance to the salinity stress and prevent or reduce a deterioration in quality of the plant which would occur if untreated. The combination can be applied prior to or during the period of salinity stress.

[0210] It should also be noted that what constitutes a salt stress condition for one plant may not be a salt stress condition for another plant.

Transplant shock hardiness

[0211] A plant that is subjected to transplanting from one growing environment to another, e.g., from a pot to flower bed or garden, can be subjected to transplant shock stress as a result of exposure to new environmental conditions such as wind, direct sun, or new soil conditions. Application of the photosensitizer compound, compositions or combinations described herein to the roots of the plant can reduce the impact to the plant caused by the transplanting. In some scenarios, stunting of plant growth and/or development of a transplanted plant can be reduced or prevented by application of the photosensitizer compound, compositions or combinations described herein.

[0212] It should be noted that what constitutes a transplant shock stress condition for one plant may not be a transplant shock stress condition for another plant.

Excess water or flooding hardiness

[0213] Although plants require a certain volume of water for healthy plant growth and development, the exposure of a plant to excess volumes of water ("water stress") can damage the plant. Application of the photosensitizer compound, compositions or combinations described herein to a plant prior to the onset of an excess water condition can increase the plant's resistance to the water stress. The photosensitizer compound, compositions or combinations described herein can be applied during the water stress, however, dilution of the photosensitizer compound, compositions or combinations described herein may occur on account of the excess water. Accordingly, pre-treatment in advance of a period of excess water can be more effective.

[0214] It should be noted that what constitutes an excess water stress condition for one plant may not be an excess water stress condition for another plant.

Insecticide activity

[0215] In some implementations, the compounds and combinations of the present description can be used to protect the plant from an insect plant pest. In should be understood that the term "insect plant pest" or "insect pest", as used herein, refers to insects and/or their larvae, which are known to or have the potential to cause damage to the plant. In some implementations, the compounds and combinations of the present description can induce photoinduced mortality in insect pest.

[0216] In some implementations, the insect pests are selected from the order of Hemiptera (groups of aphids, whiteflies, scales, mealybugs, stink bugs), Coleoptera (groups of beetles), Lepidoptera (groups of butterflies, moths), Diptera (groups of flies), Thysanoptera (group of thrips), Orthoptera (group of grasshoppers, locusts), Hymenoptera (groups of wasps, ants), Blattodea (groups of cockroaches and termites) and mite pests (spider mites).

[0217] Non-limiting examples of insect pests include: larvae of the order Lepidoptera, such as armyworms, (e.g., beet armyworm (*Spodoptera exigua*)), cutworms, loopers, (e.g., cabbage looper (*Trichoplusia ni*)) and heliothines, in the family Noctuidae (e.g., fall armyworm (*Spodoptera fugiperda* J. E. Smith)), beet armyworm (*Spodoptera exigua* Hubner), black cutworm (*Agrotis ipsilon* Hufnagel), and tobacco budworm (*Heliothis virescens* Fabricius); borers, casebearers, webworms, coneworms, cabbageworms and skeletonizers from the family Pyralidae (e.g., European corn borer (*Ostrinia nubilalis* Hubner)), navel orangeworm (*Amyelois transitella* Walker), corn root webworm (*Crambus caliginosellus* Clemens), and sod webworms (Pyralidae: Crambinae) such as sod webworm (*Herpetogramma licarsisalis* Walker), leafrollers, budworms, seed worms, and fruit worms in the family Tortricidae (e.g., codling moth (*Cydia pomonella* Linnaeus)), grape berry moth (*Endopiza viteana* Clemens), oriental fruit moth (*Grapholita molesta* Busck) and many other economically important *Lepidoptera* (e.g., diamondback moth (*Plutella xylostella* Linnaeus)), pink bollworm (*Pectinophora gossypiella* Saunders), and gypsy moth (*Lymantria dispar* Linnaeus); foliar feeding larvae and adults of the order Coleoptera including weevils from the families Anthribidae, Bruchidae, and Curculionidae (e.g., boll weevil (*Anthonomus grandis* Boheman)), rice water weevil (*Lissorhoptrus oryzophilus* Kuschel), granary weevil (*Sitophilus granarius* Linnaeus), rice weevil (*Sitophilus oryzae* Linnaeus), annual bluegrass weevil

(*Listronotus maculicollis* Dietz), bluegrass billbug (*Sphenophorus parvulus* Gyllenhal), hunting billbug (*Sphenophorus venatus* vestitus), Denver billbug (*Sphenophorus cicatristriatus* Fahraeus), flea beetles, cucumber beetles, rootworms, leaf beetles, Colorado potato beetles (*Leptinotarsa decemlineata*), and leafminers in the family Chrysomelidae, western corn rootworm (*Diabrotica virgifera virgifera* LeConte); chafers and other beetles from the family Scaribaeidae (e.g., Japanese beetle (*Popillia japonica* Newman)), oriental beetle (*Anomala orientalis* Waterhouse), northern masked chafer (*Cyclocephala borealis* Arrow), southern masked chafer (*Cyclocephala immaculate* Olivier), black turfgrass *ataenius* (*Ataenius spretulus* Haldeman), green June beetle (*Cotinis nitida* Linnaeus), Asiatic garden beetle (*Maladera castanea* Arrow), May/June beetles (*Phyllophaga* spp.) and European chafer (*Rhizotrogus majalis* Razoumowsky)); carpet beetles from the family Dermestidae; wireworms from the family Elateridae; bark beetles from the family Scolytidae; flour beetles from the family Tenebrionidae; adults and nymphs of the order Orthoptera including grasshoppers, locusts, and crickets (e.g., migratory grasshoppers (e.g., *Melanoplus sanguinipes* Fabricius, *M. differentialis* Thomas)), American grasshoppers (e.g., *Schistocerca americana* Drury), desert locust (*Schistocerca gregaria* Forskal), migratory locust (*Locusta migratoria* Linnaeus), bush locust (*Zonocerus* spp.); adults and larvae of the order Diptera including leafminers, midges, fruit flies (Tephritidae), fruit flies (e.g., *Oscinella frit* Linnaeus), soil maggots; adults and nymphs of the orders Hemiptera and Homoptera such as plant bugs from the family Miridae, leafhoppers (e.g., *Empoasca* spp.) from the family Cicadellidae; planthoppers from the families Fulgoroidae and Delphacidae (e.g., corn plant hopper (Peregrinus maidis)); treehoppers from the family Membracidae; chinch bugs (e.g., hairy chinch bug (*Blissus leucopterus* hirtus Montandon) and southern chinch bug (*Blissus insularis* Barber) and other seed bugs from the family Lygaeidae; spittlebugs from the family Cercopidae; squash bugs from the family Coreidae; red bugs and cotton stainers from the family Pyrrhocoridae; mealybugs from the family Pseudococcidae (e.g. *Planicoccus citri Risso*), cicadas from the family Cicadidae; psyllids from the family Psyllidae(e.g. Citrus psyllid *Diaphorina citri*)), whiteflies from the family Aleyrodidae (silverleaf whitefly (*Bemisia argentifolii*)); aphids from the family Aphididae, such as cotton melon aphid (*Aphis gossypii*), pea aphid (*Acyrthisiphon pisum* Harris), cowpea aphid (*Aphis craccivora* Koch), black bean aphid (*Aphis fabae* Scopoli), melon or cotton aphid (*Aphis gossypii* Glover), apple aphid (*Aphis pomi* De Geer), spirea aphid (*Aphis spiraecola* Patch), foxglove aphid (*Aulacorthum solani* Kaltenbach), strawberry aphid *Chaetosiphon fragaefolii* Cockerell), Russian wheat aphid *(Diuraphis noxia* Kurdjumov/Mordvilko), rosy apple aphid (*Dysaphis plantaginea* Paaserini), woolly apple aphid *(Eriosoma lanigerum* Hausmann), mealy plum aphid

(Hyalopterus pruni Geoffroy), turnip aphid (*Lipaphis erysimi* Kaltenbach), cereal aphid (*Metopolophium dirrhodum* Walker), potato aphid *(Macrosipum euphorbiae* Thomas), peach-potato and green peach aphid (*Myzus persicae* Sulzer), lettuce aphid (*Nasonovia ribisnigri* Mosley), root aphids and gall aphids, corn leaf aphid *(Rhopalosiphum maidis* Fitch), bird cherry-oat aphid *(Rhopalosiphum padi* Linnaeus), greenbug (*Schizaphis graminum* Rondani), English grain aphid *(Sitobion avenae* Fabricius), spotted alfalfa aphid *(Therioaphis maculata* Buckton), black citrus aphid (*Toxoptera aurantii* Boyer de Fonscolombe), brown citrus aphid (*Toxoptera citricida* Kirkaldy) and green peach aphid (*Myzus persicae*); phylloxera from the family Phylloxeridae; mealybugs from the family Pseudococcidae; scales from the families Coccidae, Diaspididae, and Margarodidae; lace bugs from the family Tingidae; stink bugs from the family Pentatomidae; adults and immatures of the order Thysanoptera including onion thrips (*Thrips tabaci* Lindeman), flower thrips (*Frankliniella* spp.), and other foliar feeding thrips. . Agronomic pests also include invertebrate arthropods sush as mites from the family Tetranychidae: twospotted spider mite (e.g. *Tetranychus urticae Koch*), flat mite from family Rutacea (e.g., citrus flat mite (*Brevipalpus lewisi* McGregor); rust and bud mites from the family Eriophyidae and other foliar feeding mites. Economically important agricultural pests nematodes (e.g., root knot nematodes in the genus *Meloidogyne,* lesion nematodes in the genus *Pratylenchus,* and stubby root nematodes in the genus *Trichodorus*) and members of the classes Nematoda, Cestoda, Trematoda, and Acanthocephala from orders of Strongylida, Ascaridida, Oxyurida, Rhabditida, Spirurida, and Enoplida.

Types of plants

[0218] The photosensitizer compounds and compositions of the present description can be used for various types of plants. The plant can be a non-woody crop plant, a woody plant or a turfgrass. The plant can be selected from the group consisting of a crop plant, a fruit plant, a vegetable plant, a legume plant, a cereal plant, a fodder plant, an oil seed plant, a field plant, a garden plant, a green-house plant, a house plant, a flower plant, a lawn plant, a turfgrass, a tree such as a fruit-bearing tree, and other plants that may be affected by microbial pathogens and/or one or more abiotic stress. Some of the compounds of the present description can display a certain degree of toxicity against a variety of noxious plant pests, in the absence or presence of light.

[0219] In some implementations, the plant is a crop plant selected from the group consisting of sugar cane, wheat, rice, corn (maize), potatoes, sugar beets, barley, sweet potatoes, cassava, soybeans, tomatoes, and legumes (beans and peas).

[0220] In other implementations, the plant is a tree selected from the group consisting of deciduous trees and evergreen trees. Examples of trees include, without limitation, maple trees, fruit trees such as citrus trees, apple trees, and pear trees, an oak tree, an ash tree, a pine tree, and a spruce tree.

[0221] In yet other implementations, the plant is a shrub.

[0222] In yet other implementations, the plant is a fruit or nut plant. Non-limiting examples of such plants include: acerola (barbados cherry), atemoya, carambola (star fruit), rambutan, almonds, apricots, cherries, nectarines, peaches, pistachio, apples, avocados, bananas, plantains, figs, grapes, mango, olives, papaya, pears, pineapple, plums, strawberries, grapefruit, lemons, limes, oranges (e.g., navel and Valencia), tangelos, tangerines, mandarins and plants from the berry and small fruits plant group.

[0223] In other implementations, the plant is a vegetable plant. Non-limiting examples of such plants include: asparagus, bean, beets, broccoli, Chinese broccoli, broccoli raab, brussels sprouts, cabbage, cauliflower, Chinese cabbage (e.g., bok choy and mapa), Chinese mustard cabbage (gai choy), cavalo broccoli, collards, kale, kohlrabi, mizuna, mustard greens, mustard spinach, rape greens, celery, chayote, Chinese waxgourd, citron melon, cucumber, gherkin, hyotan, cucuzza, hechima, Chinese okra, balsam apple, balsam pear, bitter melon, Chinese cucumber, true cantaloupe, cantaloupe, casaba, crenshaw melon, golden pershaw melon, honeydew melon, honey galls, mango melon, Persian melon, pumpkin, summer squash, winter squash, watermelon, dasheen (taro), eggplant, ginger, ginseng, herbs and spices (e.g., curly leaf basil, lemon balm, cilantro, Mexican oregano, mint), Japanese radish (daikon), lettuce, okra, peppers, potatoes, radishes, sweet potatoes, Chinese artichoke (Japanese artichoke), corn and tomatoes.

[0224] In other implementations, the plant is a flowering plant, such as roses, flowering shrubs or ornamentals. Non-limiting examples of such plants include: flowering and foliage plants including roses and other flowering shrubs, foliage ornamentals & bedding plants, fruit-bearing trees such as apple, cherry, peach, and pear trees, non-fruit-bearing trees, shade trees, ornamental trees, and shrubs (e.g., conifers, deciduous and broadleaf evergreens & woody ornamentals).

[0225] In some implementations, the plant is a houseplant. Non-limiting examples of such plants include: chrysanthemum, dieffenbachia, dracaena, ferns, gardenias, geranium, jade plant, palms, philodendron, and schefflera.

[0226] In some implementations, the plant is a plant grown in a greenhouse. Non- limiting examples of such plants include: ageratum, crown of thorns, dieffenbachia, dogwood, dracaena, ferns, ficus, holly, lisianthus, magnolia, orchid, palms, petunia, poinsettia, schefflera, sunflower, aglaonema, aster, azaleas, begonias, browallia, camellias, carnation, celosia, chrysanthemum, coleus, cosmos, crepe myrtle, dusty miller, easter lilies, fuchsia, gardenias, gerbera, hellichrysum, hibiscus foliage, hydrangea, impatiens, jade plant, marigold, new guinea, impatiens, nicotonia, philodendron, portulaca, reiger begonias, snapdragon, and zinnias.

Synergistic effect of the combinations

[0227] In some scenarios, the combinations can exhibit a synergistic response for inhibiting growth of microbial pathogens in plants. It should be understood that the terms “synergy” or “synergistic”, as used herein, refer to the interaction of two or more components of a combination (or composition) so that their combined effect is greater than the sum of their individual effects. This may include, in the context of the present description, the action of two or more of the nitrogen-bearing macrocyclic compounds, the oil, and the chelating agent. In some scenarios, the nitrogen-bearing macrocyclic compound and the oil can be present in synergistically effective amounts. In some scenarios, the nitrogen-bearing macrocyclic compound and the chelating agent can be present in synergistically effective amounts. In some scenarios, the oil and the chelating agent can be present in synergistically effective amounts. In some scenarios, the nitrogen-bearing macrocyclic compound, the oil and the chelating agent can be present in synergistically effective amounts.

[0228] In some scenarios, the approach as set out in S. R. Colby, “Calculating synergistic and antagonistic responses of herbicide combinations”, Weeds 15, 20-22 (1967), can be used to evaluate synergy. Expected efficacy, E, may be expressed as: $E=X+Y(100-X)/100$, where X is the efficacy, expressed in % of the untreated control, of a first component of a combination, and Y is the efficacy, expressed in % of the untreated control, of a second component of the combination. The two components are said to be present in synergistically effective amounts when the observed efficacy is higher than the expected efficacy.

EXAMPLES

[0229] Some abbreviations and acronyms are used in the description of the experimental procedures and Examples below. Although most of these abbreviations and acronyms would be understood by a person skilled in the art, Table A contains a list of most of these abbreviations and acronyms.

Table A. List of abbreviations and acronyms

Abbreviation	Meaning
Ac_2O	Acetic anhydride
DCM	Dichloromethane
rt	Room temperature
DMAE	Dimethylaminoethyl
BAE	Butylaminoethyl
DMAB	Dimethylaminobutyl
DEAEAE	Diethylaminoethyl aminoethyl
C_4	*n*-butyl
C_{12}	*n*-dodecyl
Tf	Triflate
TMEA	Trimethylammonium ethyl
EP OA	Ethylphosphate octylammonium
T(TMS)SP	Tris(trimethylsiloxy)silylpropyl
3TP	3-thiapentanyl
4-DMAP	4-Dimethylaminopyridine
Boc_2O	Di-tert-butyldicarbonate
AcN	Acetonitrile

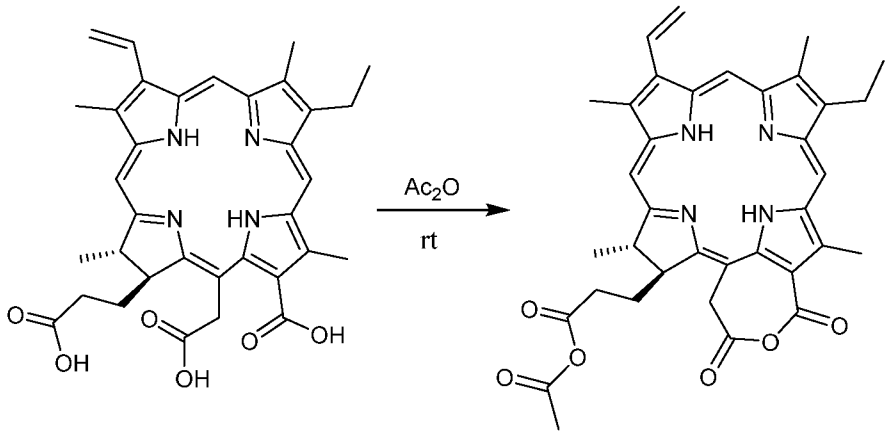
Preparation of Compounds

[0230] Chlorin e6 (Ce6) was purchased from Frontier Scientific, acetic anhydride was purchased from Caledon; di-tert-butyldicarbonate, copper(II) acetate, zinc acetate, 99.99%, palladium(II) acetate, chlorotrimethylsilane, MeI, potassium carbonate, sodium bicarbonate, N-(*n*-butyl)ethylenediamine (97%), N,N-dimethylbutanediamine (98%), N,N-diethyldiethylenetriamine (98%), *n*-butylamine, dodecylamine, (2-aminoethyl)trimethylammonium chloride hydrochloride (DMAE•HCl), poly(ethylene glycol) monooleate (MW 860), and lanthanum(III) triflate were purchased from Sigma-Aldrich; (3-

aminopropyl)tris(trimethylsiloxy)silane was purchased from Gelest, polyethylene glycol monoallyl ether was received from Clariant, α-hydroxy-poly(ethylene glycol)-ω-(ethylthio)ethylamine was received from Enroute Interfaces. All chemicals were used as received. Solvents used in this study were purchased from Caledon and dried by passing through an activated alumina column under a nitrogen stream before use. Reported yields are mass balances assuming a 1:1 mixture of mono- and di-functonal products.

[0231] ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker AV-600 (at 600.13 MHz for protons, at 150.9 MHz for carbon, respectively). Electrospray ionization mass spectrometry (ESI-MS) was performed using a Agilent 6340 Ion Trap mass spectrometer.

Compound 1 (Ce6-Ac^{17}-Cycl^{13,15} dianhydride)



Ce6 1

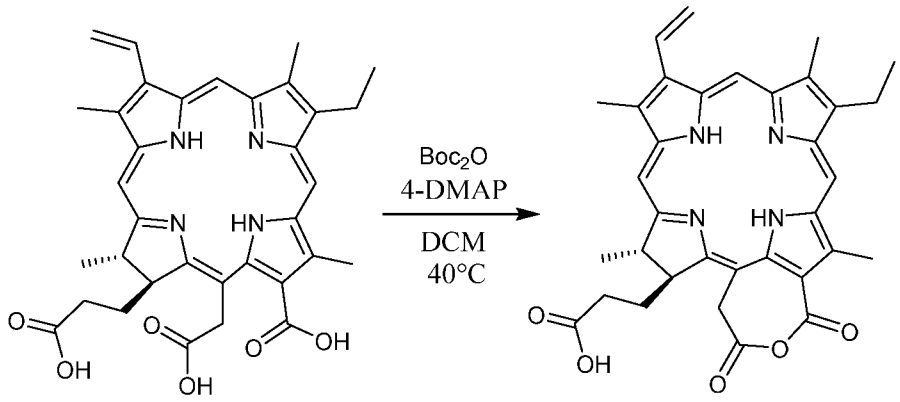
[0232] Chlorin e6 (Ce6) (0.261, g, 0.44 mmol) was suspended in dry acetic anhydride (44 mL). The reaction mixture was stirred for 20 h at room temperature in the absence of ambient light. Acetic acid and volatile organics were removed at 45°C under reduced pressure. The residue was suspended in dichloromethane (DCM, 20 mL) and filtered. After removing DCM under reduced pressure, 0.250 g of compound 1 was obtained as a dark purple solid (91% yield).

[0233] ^{1}H NMR (δ, 600.13 MHz, CD_2Cl_2): -0.65 (br, 1H), -0.53 (br, 1H), 1.24 (m, 3H), 1.57 (m, 3H), 1.66 (d, 3H, J=7.0 Hz), 2.00 (s, 2H), 2.02 (m, 1H), 2.28 (m, 1H), 2.57 (m, 1H), 2.64 (m, 1H), 3.07 (s, 3H), 3.28 (s, 3H), 3.56 (m, 2H), 3.59 (s, 3H), 4.10 (m, 1H), 4.32 (m, 1H), 4.45 (m, 1H), 5.27 (m, 2H), 6.06 (d, 1H, J=11.6 Hz), 6.23 (d, 1H, J=17.8 Hz), 7.85 (m, 1H), 8.49 (s, 1H), 9.20 (s, 1H) and 9.48 (s, 1H) ppm.

[0234] ^{13}C NMR (δ, 150.9 MHz, CD_2Cl_2): 11.1, 11.2, 12.1, 17.5, 19.6, 22.4, 23.4, 24.2, 29.4, 30.8, 32.3, 39.2, 40.7, 49.4, 52.3, 94.1, 99.0, 99.1, 104.7, 117.1, 122.9, 128.9, 129.1, 129.4, 131.3, 132.8, 125.5, 136.4, 136.5, 137.8, 141.4, 142.7, 146.4, 149.7, 157.6, 160.9, 165.7, 166.3, 166.8, 168.0 and 174.3 ppm.

[0235] MS-ESI (HRMS) m/z calculated for C36H37N4O6, ($M+H^+$): 621.2635. Found: 621.2708.

Compound 2 (Ce6-Cycl^{13,15} anhydride)

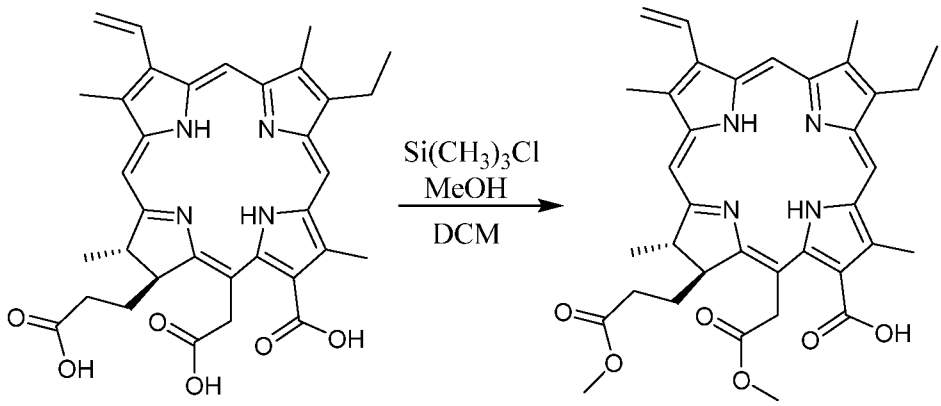


Ce6 **2**

[0236] A mixture of Ce6 (0.255 g, 0.427 mmol), di-tert-butyldicarbonate (0.099 g, 0.441 mmol) and 4-Dimethylaminopyridine (0.004 g, 0.036 mmol) in DCM (30 mL) was heated at 40°C for 2 h. The reaction mixture was filtered, and solvent and volatiles were removed at 40°C under reduced pressure, the resulting solid was washed with hexane (3 x 10 mL) then dried *in vacuo* to give compound 2, 0.253 g, 89% yield.

[0237] MS-ESI (HRMS) m/z calculated for C34H35N4O5 ($M+H^+$): 579.2602. Found: 579.2600.

Compound 3a (Ce6-di-Methyl^{15,17} ester)



Ce6 3a

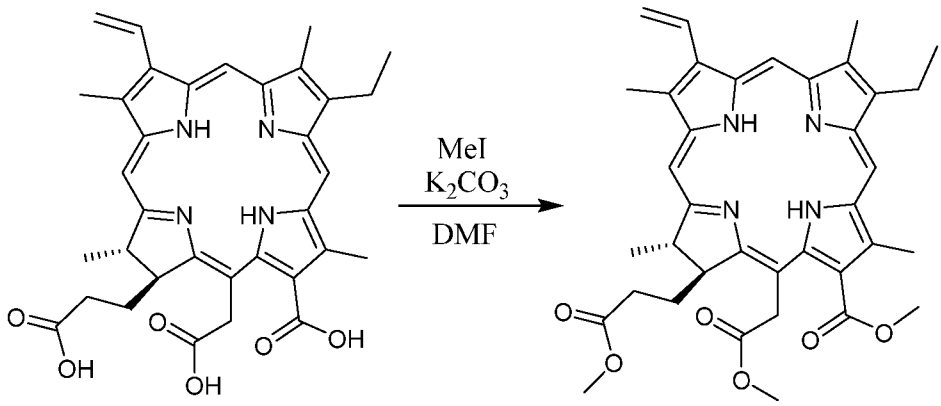
[0238] To a suspension of Ce6 (1.001 g, 1.678 mmol) in DCM (20 mL) chlorotrimethylsilane (1.185 g, 10.906 mmol) was added slowly at room temperature, the mixture was stirred at room temperature for 5 min, then methanol (7 mL) was added slowly. After stirring at room temperature overnight, the mixture was concentrated under reduced pressure to about 5 mL, precipitated into diethyl ether (20 mL). The precipitate was washed with ether (10 mL x3), and dried *in vacuo*, to obtain compound 3a (Ce6-di-methyl^{15,17} ester) (0.946 g, 90% yield).

[0239] ^{1}H NMR (δ, 600.13 MHz, $CDCl_3$): 1.50 (m, 6H), 2.13 (m, 2H), 2.32 (m, 1H), 3.06-3.32 (m, 12H), 3.38 (m, 2H), 3.57 (m, 3H), 3.66 (s, 3H), 4.14 (m, 3H), 4.65 (br, 2H), 4.96 (br, 2H), 6.05 (m, 2H), 7.61 (m, 1H), 8.35 (s, 1H), 9.33 (s, 1H), 9.55 (s, 1H) ppm.

[0240] ^{13}C NMR (δ, 150.9 MHz, $CDCl_3$): ^{13}C NMR (δ, 150.9 MHz, $CDCl_3$): 11.3, 12.3, 13.17, 16.6, 19.6, 23.2, 27.4, 30.4, 39.9, 47.9, 49.8, 51.9, 52.8, 93.1, 101.1, 108.0, 122.1, 125.5, 128.0, 133.1, 133.2, 133.8, 134.4, 136.7, 139.0, 141.3, 143.8, 168.0, 169.6, 169.7, 172.0, 173.3 ppm.

[0241] MS-ESI (HRMS) m/z calculated for C36H41N4O6 (M+H+): 625.3021. Found: 625.3031.

Compound 3b (Ce6-tri-Methyl^{13,15,17} ester)



Ce6 3b

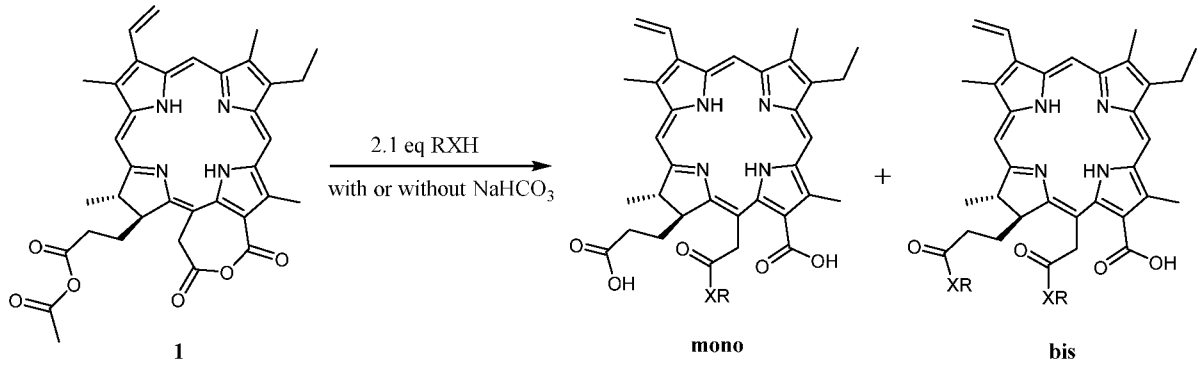
[0242] To a DMF (40 mL) solution of Chlorin e6 (1.990 g, 3.34 mmol) was added potassium carbonate (23.070 g, 166.92 mmol); MeI (4.739 g, 33.38 mmol) was added dropwise. After the reaction mixture was stirred at room temperature overnight under N_2 in the absence of ambient light overnight, a saturated aq. NH_4Cl solution (30 mL), was added. The resulting mixture was then extracted with DCM (20 mL x 3) and the combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, filtered, concentrated *in vacuo*, and precipitated into MeOH. The resulting precipitate was filtered and dried *in vacuo* to give pure compound 3b (Ce6-tri-methyl ester) (1.753 g, 82% yield).

[0243] ^1H NMR (δ, 600.13 MHz, $CDCl_3$): -1.56 (s, 1H), -1.42 (s, 1H), 1.58 (m, 3H), 1.67 (m, 3H), 2.12 (m, 2H), 2.47 (m, 1H), 3.15 (s, 3H), 3.34 (s, 3H), 3.48 (s, 3H), 3.53 (s, 3H), 3.63 (m, 2H), 3.68 (s, 3H), 4.16 (s, 3H), 4.33 (m, 2H), 5.15 (d, 1H, J=18.9 Hz), 5.26 (d, 1H, J=19.0 Hz), 6.00 (d, 1H, J=14.5 Hz), 6.20 (d, 1H, J=17.9 Hz), 7.90 (m, 1H), 8.64 (s, 1H), 9.41 (s, 1H), 9.57 (s, 1H) ppm.

[0244] ^{13}C NMR (δ, 150.9 MHz, $CDCl_3$): 11.3, 12.2, 12.4, 17.7, 19.7, 23.0, 29.6, 31.1, 49.4, 51.7, 52.2, 53.0, 53.1, 93.6, 102.2, 102.3, 121.8, 123.6, 129.4, 130.6, 134.8, 135.4, 135.5, 135.9, 136.5, 139.5, 145.0, 148.9, 154.8, 167.0, 169.5, 169.6, 173.1, 173.6.

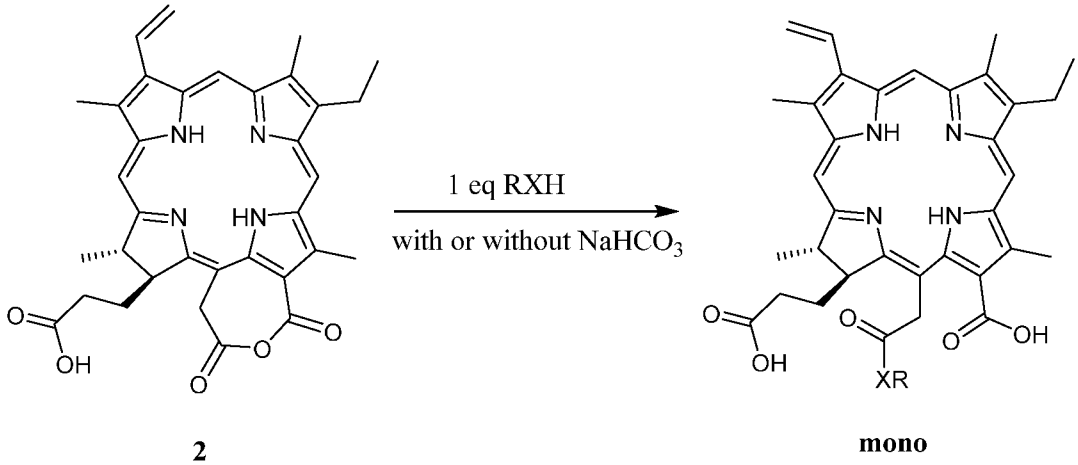
[0245] MS-ESI (HRMS) m/z calculated for C37H43N4O6 ($M+H^+$): 639.3177. Found: 639.3169.

General procedure A



[0246] Following the procedure for the synthesis of Ce6-bis-anhydride (Compound 1), after acetic anhydride and volatile organics were removed *in vacuo*, the resulting Ce6-bis-anhydride (a dark solid) was re-dissolved in DCM and filtered, the corresponding amine or alcohol compound RXH (X = NH or O, 2.1 eq.), was added. The mixture was allowed to stir at room temperature overnight in the absence of ambient light. The reaction mixture was filtered, concentrated and precipitated into diethyl ether. The precipitation step was repeated twice, the resulting precipitate was isolated by filtration, washed with diethyl ether (5 mL x 2), then dried *in vacuo*.

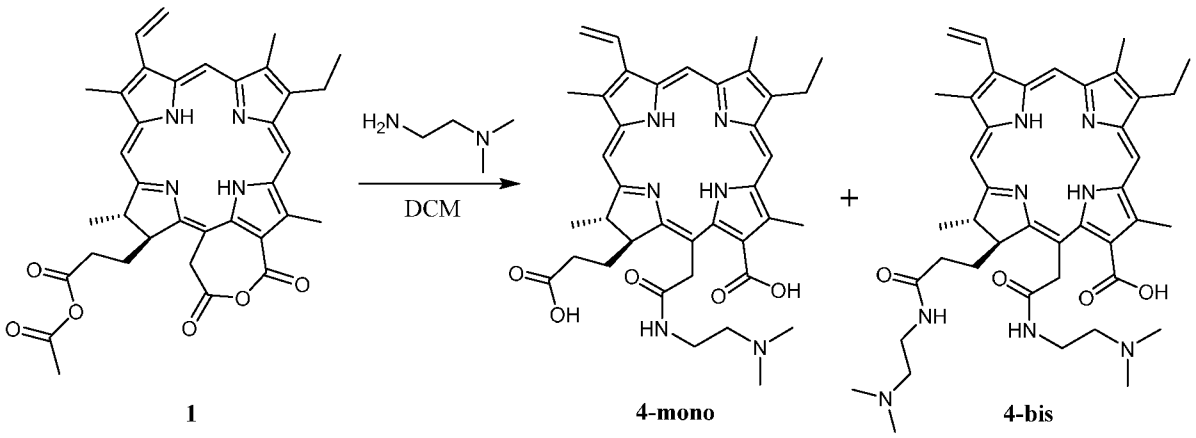
General procedure B



[0247] Following the procedure of synthesis of Ce6-mono-anhydride (Compound **2**), after washing with hexane the resulting Ce6-mono-anhydride was re-dissolved in DCM (20 mL), the corresponding amine or alcohol (RXH, X = NH or O, 1 eq.) was added. The mixture was allowed to stir at room temperature for 4 h in the absence of ambient light. The reaction

mixture was concentrated and precipitated in diethyl ether, the precipitate was isolated by filtration, washed with ether (5 mL x 2), the precipitate was dissolved in DCM (10 mL), the DCM solution was filtered, the precipitate was washed with DCM (5 mL) twice. The combined DCM solution was evaporated under reduced pressure then dried *in vacuo*.

Compound 4-mix (Ce6-mix-DMAE^{15,17} amide)



1 4-mono 4-bis

[0248] Following general procedure A, Ce6 (4.9447 g, 8.30 mmol), acetic anhydride (60 mL, 634.7 mmol), N,N-dimethylethylenediamine (3.0712 g, 33.2 mmol) were used as reactants. Compound 4-mix was obtained as a mixture of compound 4-mono (Ce6-mono-DMAE^{15} amide) and compound 4-bis (Ce6-di-DMAE^{15,17} amide) (94% yield) in a ratio of 1.46:1 based on the result of LC-UV-HRMS(ESI).

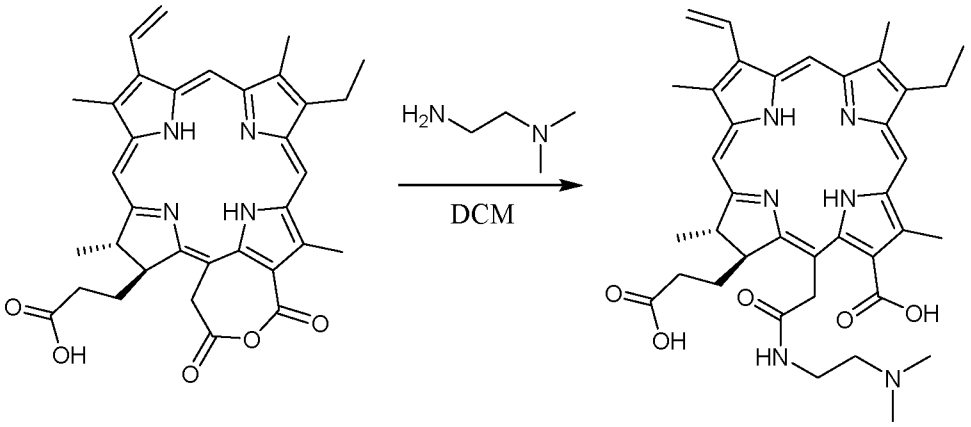
[0249] ^{1}H NMR (δ, 600.13 MHz, $CDCl_3$): ^{1}H NMR (δ, 600.13 MHz, $CDCl_3$): -2.14 (br, 1H), -1.90 (br, 1H), 1.67-1.73 (m, 6H), 1.93-2.11 (m, 9H), 2.25-2.33 (m, 5H), 2.60-2.75 (m, 5H), 3.35 (m, 3H), 3.46 (m, 3H), 3.60 (m, 3H), 3.82 (m, 2H), 4.47-4.50 (m, 2H), 6.15 (d, 1H, J=11.6 Hz), 6.37 (d, 1H, J=17.8 Hz), 8.13 (m, 1H), 8.82, 8.85 (s, 1H), 9.66, 9.67, 9.70 (s, 2H) ppm.

[0250] ^{13}C NMR (δ, 150.9 MHz, $CDCl_3$): 11.39, 12.16, 15.29, 17.79, 19.71, 23.03, 23.29, 23.33, 30.76, 31.06, 37.40, 39.25, 39.83, 42.71, 43.29, 43.88, 44.75, 45.35, 49.05, 49.21, 53.22, 56.55, 58.06, 93.65, 93.66, 98.80, 100.0, 100.3, 103.4, 121.3, 129.33, 129.5, 129.7, 131.0, 132.5, 132.8, 133.7, 133.8, 133.9, 134.0, 134.3, 134.5, 135.5, 136.06, 136.13, 137.8, 137.9, 144.1, 144.2, 149.1, 152.9, 153.0, 168.5, 172.8, 175.4, 177.0, 179.2 ppm.

[0251] Ce6-mono-DMAE^{15} amide: MS-ESI (HRMS) m/z calculated for C38 H47 N6 O5 ($M+H^+$): 667.3602. Found: 667.3604.

[0252] Ce6-di-DMAE^{15,17} amide: MS-ESI (HRMS) m/z calculated for C42 H57 N8 O4 ($M+H^+$): 737.4497. Found: 737.4495.

Compound 4-mono (Ce6-mono-DMAE^{15} amide)



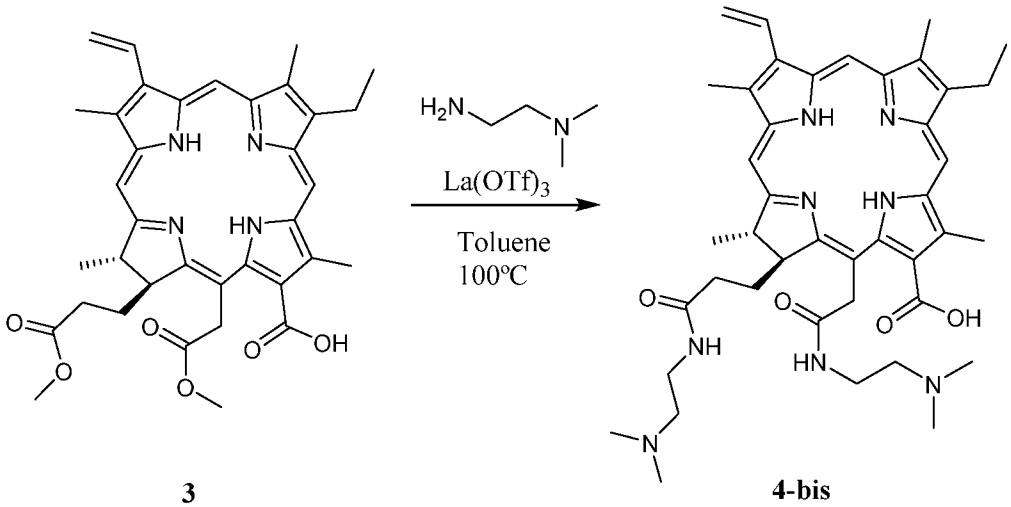
2 **4-mono**

[0253] Following general procedure B, Ce6 (0.254 g, 0.427 mmol) di-tert-butyldicarbonate (0.099 g, 0.441 mmol), 4-dimethylaminopyridine (0.004 g, 0.036 mmol) and N,N-dimethylethylenediamine (0.040 g, 0.427 mmol) were used. Ce6-mono-DMAE^{15} amide as dark green solid was obtained (0.264 g, 93% yield).

[0254] ^{1}H NMR (δ, 600.13 MHz, $CDCl_3$): -2.37 (s, 1H), -1.99 (br, 1H), 1.67 (m, 6H), 1.93-2.11 (m, 6H), 2.22 (m, 2H), 2.37 (m, 2H), 2.51 (m, 2H), 2.74 (br, 2H), 3.30 (s, 3H), 3.50 (m, 6H), 3.75 (s, 2H), 4.46 (br, 2H), 5.33 (br, 1H), 5.86 (br, 1H), 6.14 (d, 2H, J=11.2 Hz), 6.35 (d, 2H, J=17.8 Hz), 8.11 (m, 1H), 8.23 (s, 1H), 9.59 (s, 1H), 9.65 (s, 1H) ppm.

[0255] Ce6-mono-DMAE^{15} amide, MS-ESI (HRMS) m/z calculated for C38 H47 N6 O5, ($M+H^+$): 667.3602. Found: 667.3600.

Compound 4-bis (Ce6-bis-DMAE^{15,17} amide)



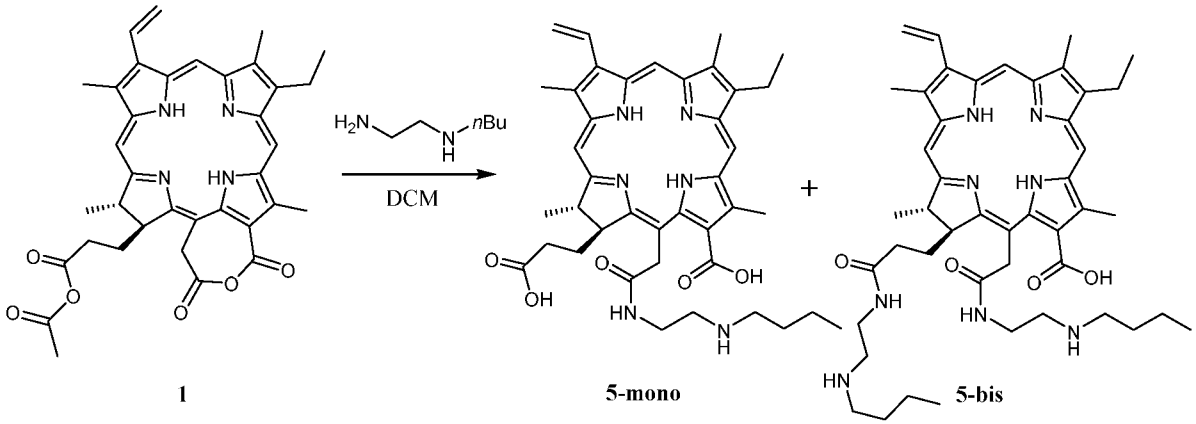
3 4-bis

[0256] Compound 3 Ce6-di-methyl^{15,17} ester (0.200 g, 0.320 mmol), N,N-dimethylethylenediamine (0.0612 g, 0.65 mmol) and lanthanum(III) triflate (0.0192 g, 0.032 mmol) in toluene (50 mL) was heated at 100°C for 24h. The reaction mixture was concentrated under reduced pressure to *ca.* 5 mL and cooled down to room temperature, the resulting precipitate was collected by filtration, washed with toluene (2 mLx2) and dried *in vacuo* giving Ce6-di-DMAE^{15,17} amide as dark green solid (0.215 g, 91%).

[0257] ^{1}H NMR (δ, 600.13 MHz, DMSO): -2.30 (s, 1H), -1.90 (s, 1H), 1.69-1.72 (m, 6H), 2.19 (m, 12H), 2.23 (m, 2H), 2.45 (m, 4H), 2.67 (m, br, 2H,), 2.88 (m, 4H), 3.34 (s, 3H), 3.52 (s, 3H), 3.56 (s, 3H), 3.83 (m, 2H), 4.49 (m, 1H), 4.60 (m, 1H), 6.18 (d, 1H, J=11.6 Hz), 6.47 (d, 1H, J=17.9 Hz), 8.36 (m, 1H), 9.10 (s, 1H), 9.69 (s, 1H), 9.78 (s, 1H) ppm.

[0258] Ce6-di-DMAE^{15,17} amide: MS-ESI (HRMS) m/z calculated for C42 H57 N8 O4 (M+H$^+$): 737.4497. Found: 737.4504.

Compound 5-mix (Ce6-mix-BAE^{15,17} amide)



[0259] Following the general procedure A, Compound 1 (0.300 g, 0.484 mmol) was dissolved in DCM (20 mL) and N-(*n*-butyl)ethylenediamine (0.115 g, 0.967 mmol) was added. Compound 5-mix was obtained as a mixture of 5-mono (Ce6-mono-BAE^{15} amide) and 5-bis (Ce6-di-BAE^{15,17} amide) as a dark green solid (0.324 g, 90% yield).

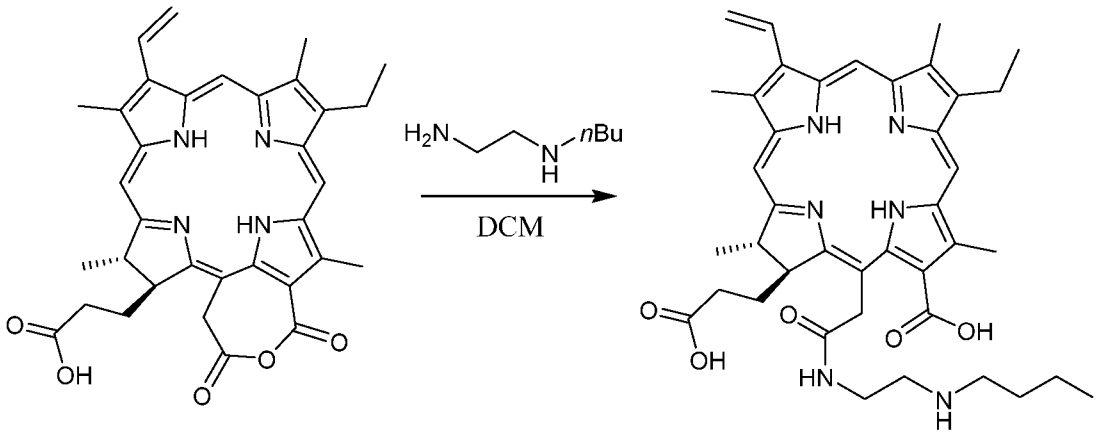
[0260] ^{1}H NMR (δ, 600.13 MHz, $CDCl_3$): -2.26 (br, 1H), -1.95 (br, 1H), 0.76 (m, 3H), 1.20-1.37 (m, 4H), 1.64 (m, 6H), 2.07-2.30 (m, 2H), 2.40-2.77 (m, 6H), 3.22 (m, 3H), 3.39 (m, 3H), 3.48 (m, 3H), 3.71 (m, 2H), 4.41 (m, br, 2H), 5.52 (br, 2H), 6.01 (d, 1H, J=10.7), 6.24 (m, 1H), 8.00 (m, 1H), 8.85 (s, 1H), 9.60 (br, 2H) ppm.

[0261] ^{13}C NMR (δ, 150.9 MHz, $CDCl_3$): 11.4, 12.1, 12.2, 13.4, 13.7, 17.8, 19.8, 20.2, 22.7, 23.2, 23.5, 27.6, 27.8, 30.9, 31.3, 34.2, 36.5, 39.6, 39.9, 45.0, 46.8, 47.0, 47.5, 48.1, 48.8, 53.5, 94.1, 99.0, 100.4, 102.3, 121.3, 129.4, 129.7, 131.2, 132.5, 133.9, 134.0, 134.2, 135.2, 136.2, 138.1, 144.2, 149.3, 153.1, 168.7, 169.4, 175.8, 176.0, 177.4, 180.7 ppm.

[0262] Ce6-mono-BAE^{15} amide, MS-ESI (HRMS) m/z calculated for C40 H51 N6 O5, ($M+H^+$): 695.3915. Found: 695.3916.

[0263] Ce6-di-BAE^{15,17} amide, MS-ESI (HRMS) m/z calculated for C46 H65 N8 O4, ($M+H^+$): 793.5123. Found: 793.5121.

Compound 5-mono (Ce6-mono-BAE[15] amide)



2 **5-mono**

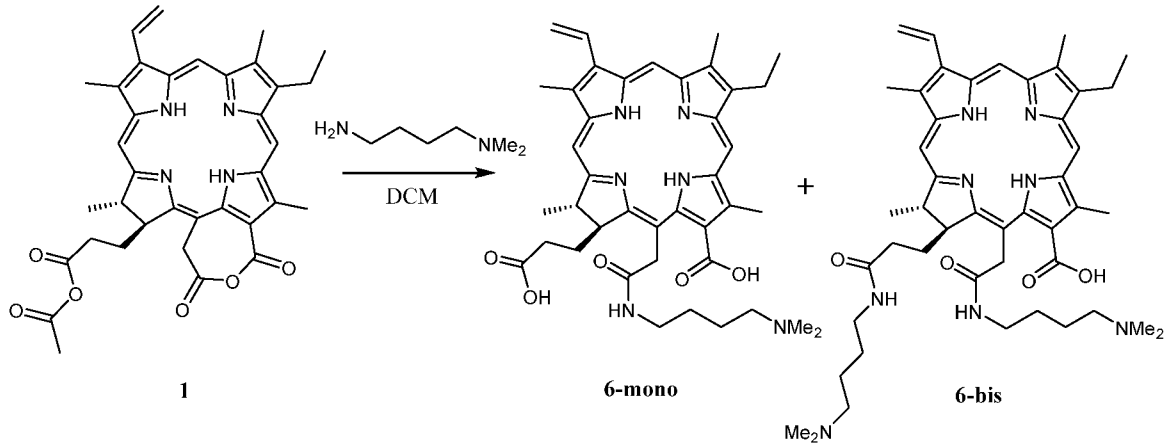
[0264] Following general procedure B, Ce6 (0.318 g, 0.533 mmol) di-tert-butyldicarbonate (0.118 g, 0.540 mmol), 4-dimethylaminopyridine (0.003 g, 0.025 mmol) and N-(n-butyl)ethylenediamine (0.064 g, 0.533 mmol) were used. Ce6-mono-BAE[15] amide as dark green solid was obtained (0.322 g, 87% yield).

[0265] ^{1}H NMR (δ, 600.13 MHz, $CDCl_3$): -2.33 (s, 1H), -1.99 (br, 1H), 0.68 (m, 3H), 1.20 (br, 2H), 1.37 (br, 2H), 1.61 (br, 6H), 2.19 (m, 2H), 2.41 (m, 2H), 2.76 (m, 4H), 3.22 (m, 3H), 3.38 (m, 3H), 3.48 (m, 3H), 3.70 (m, 2H), 4.37 (br, 1H), 4.44 (br, 1H), 5.49 (br, 2H), 6.01 (d, 1H, J=10.7), 6.23 (m, 1H, J=17.4), 8.01 (m, 1H), 8.78 (s, 1H), 9.59 (br, 2H) ppm.

[0266] ^{13}C NMR (δ, 150.9 MHz, $CDCl_3$): 11.4, 12.0, 12.2, 13.2, 13.7, 17.7, 19.5, 19.7, 20.1, 23.5, 27.5, 30.4, 32.9, 36.6, 39.6, 44.7, 46.7, 47.6, 48.8, 53.3, 94.0, 99.0, 100.3, 102.4, 121.2, 128.6, 129.3, 129.7, 131.4, 132.5, 133.7, 133.9, 134.3, 135.3, 136.1, 137.9, 144.1, 149.4, 153.0, 168.2, 169.0, 175.5, 175.9, 180.2 ppm.

[0267] Ce6-mono-BAE[15] amide, MS-ESI (HRMS) m/z calculated for C40 H51 N6 O5, ($M+H^+$): 695.3915. Found: 695.3916.

Compound 6-mix (Ce6-mix-DMAB^{15,17} amide)



[0268] Following general procedure A, Ce6-bis-anhydrides (0.306 g, 0.493 mmol) was dissolved in DCM (20 mL) and N,N-dimethylbutanediamine (0.117 g, 0.988 mmol) was added. Compound 6-mix was obtained as a mixture of 6-mono (Ce6-mono-DMAB^{15} amide) and 6-bis (Ce6-di-DMAB^{15,17} amide) as a dark green solid (0.345 g, 94% yield).

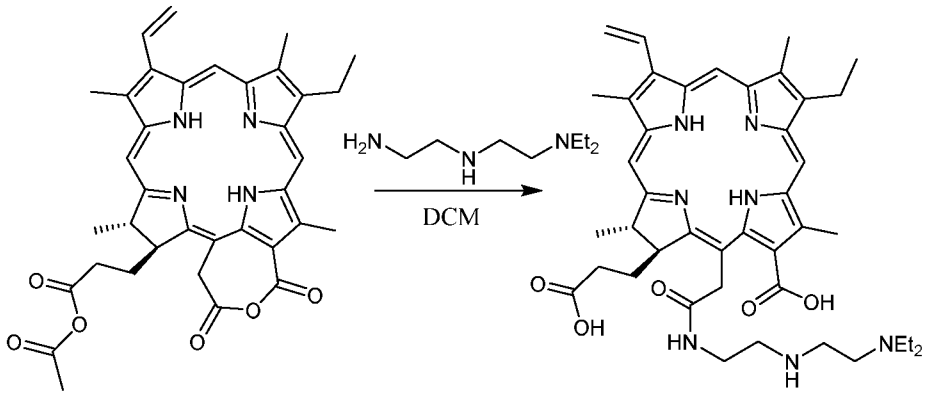
[0269] ^{1}H NMR (δ, 600.13 MHz, $CDCl_3$): 1.533-1.82 (m, 18H), 1.91 (m, 4H), 2.15 (m, 2H), 2.28 (m, 3H), 2.25-3.02 (m, 5H), 3.21 (s, 3H), 3.37-3.52 (m, 6H), 3.66 (m, 2H), 4.32-4.53 (m, 2H), 6.05 (d, 1H, J=11.6 Hz), 6.25 (d, 1H, J=17.6Hz), 8.02 (m, 1H), 8.79 (s, 1H), 9.55 (s, 1H), 9.59 (s, 1H) ppm.

[0270] ^{13}C NMR (δ, 150.9 MHz, $CDCl_3$): 11.2, 12.1, 17.7, 19.5, 21.5,21.7, 22.2, 22.3, 23.4, 23.5, 23.6, 24.5, 26.0, 26.3, 31.2, 34.6, 38.3, 38.7, 39.2, 41.8, 42.2, 42.7, 42.8, 48.5, 49.2, 53.3, 55.8, 56.6, 57.0, 94.1, 98.7, 99.6, 99.9, 103.5, 121.3, 129.2, 129.5, 131.0, 132.6, 132.8, 133.4, 133.5, 133.7, 133.8, 134.9, 135.2, 136.2, 137.5, 144.0, 149.0, 152.6, 152.8, 168.3, 173.8, 175.3, 177.5, 179.5 ppm.

[0271] Ce6-mono-DMAB^{15} amide, MS-ESI (HRMS) m/z calculated for C40 H51 N6 O5 ($M+H^+$): 695.3915. Found: 695.3913.

[0272] Ce6-di-DMAB^{15,17} amide, MS-ESI (HRMS) m/z calculated for C46 H65 N8 O4, ($M+H^+$): 793.5123. Found: 793.5125.

Compound 7-mono (Ce6-mono-DEAEAE[15] amide)



1 7-mono

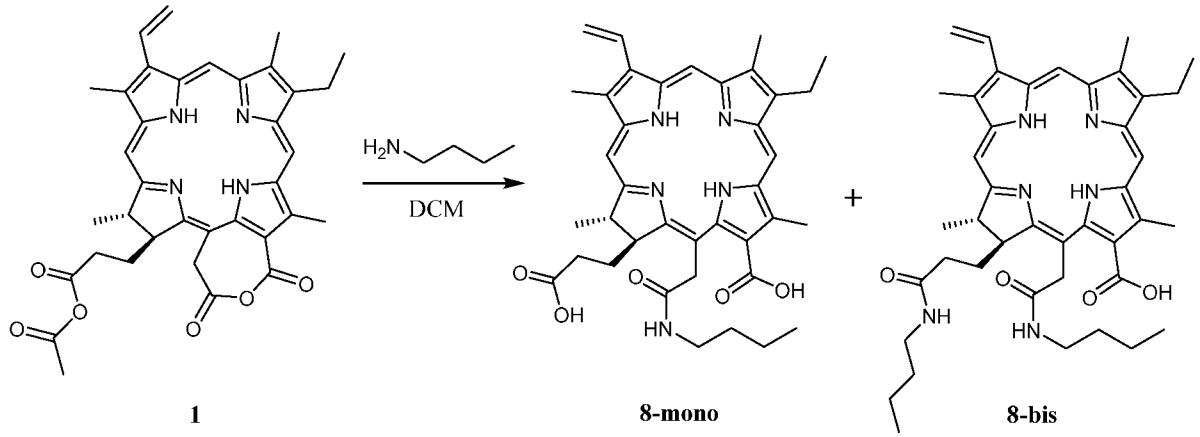
[0273] Following general procedure A, compound 1 (0.578 g, 0.932 mmol) in DCM (20 mL) and N,N-diethyldiethylenetriamine (98%) (0.303 g, 1.865 mmol) were used. The crude compound 7-mix (mixture of Ce6-mono-DEAEAE[15] amide and Ce6-bis-DEAEAE[15,17] amide) obtained was subjected to workup. Compound 7-mono (Ce6-mono-DEAEAE[15] amide) was the only product isolated after workup. Compound 7-mono was isolated as dark green solid was obtained (0.422 g, 56% yield).

[0274] ^{1}H NMR (δ, 600.13 MHz, $CDCl_3$): -2.36 (br, 1H), -2.02 (br, 1H), 1.04 (m, 6H), 1.64-1.73 (m, 6H), 1.98-2.27 (m, 2H), 2.37-2.80 (m, 6H), 2.53 (m, 2H), 3.09-3.55 (13H), 3.66 (br, 4H), 4.38 (m, 2H), 5.30 (br, 2H), 6.01 (m, 2H), 6.23 (m, 2H), 7.61 (m, 1H), 8.01 (m, 1H), 8.76 (s, 1H), 9.56 (s, 1H) ppm.

[0275] ^{13}C NMR (δ, 150.9 MHz, $CDCl_3$): 10.2, 11.4, 11.8, 12.2, 17.8, 19.7, 23.4, 31.2, 34.2, 36.8, 39.7, 45.5, 46.6, 48.6, 49.0, 51.8, 53.5, 94.0, 100.1, 121.3, 129.3, 131.2, 132.6, 133.6, 133.9, 135.5, 136.1, 137.8, 144.1, 149.2, 152.8, 168.6, 171.1, 175.5, 176.8, 179.5 ppm.

[0276] Ce6-mono-DEAEAE[15] amide, MS-ESI (HRMS) m/z calculated for C42 H56 N7 O5 (M+H+): 738.4337. Found: 738.4350.

Compound 8-mix (Ce6-mix-$C_4^{15,17}$ amide)



1 **8-mono** **8-bis**

[0277] Following general procedure A, compound 1 (0.301 g, 0.486 mmol), *n*-butylamine (0.0746 g, 0.102 mmol) and $NaHCO_3$, 0.2024 g (2.528 mmol) were used. A mixture 8-mix of compound 8-mono (Ce6-mono-C4 ^{15} amide) and compound 8-bis (Ce6-bis-C4 ^{15,17} amide) was obained as a dark solid (0.295 g, 90% yield).

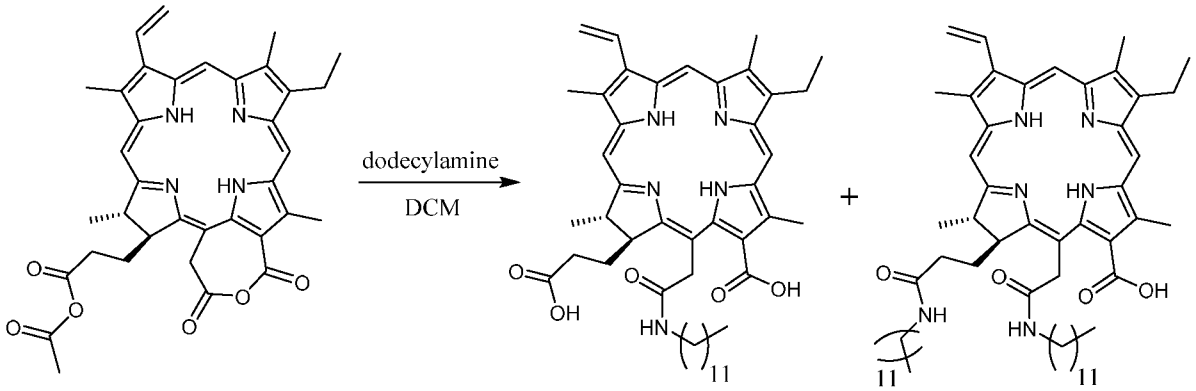
[0278] ^{1}H NMR (δ, 600.13 MHz, $CDCl_3$): -1.92 (br, 1H), -2.14 (s, 1H), 0.93-1.25 (m, 9H), 1.57-1.63 (m, 5H), 1.71-1.75 (m, 5H), 2.17-2.26 (m, 2H), 2.69-2.79 (m, 2H), 2.79-2.98 (m, 4H), 3.36 (m, 3H), 3.53 (m, 3H), 3.66 (m, 3H), 3.83 (m, 2H), 4.51 (m, 2H), 6.16 (d, 2H, J=11.6), 6.38 (d, 2H, J=17.8), 8.15 (m, 1H), 8.87, 8.88 (s, 1H), 9.74, 9.75 (s, 1H) ppm.

[0279] ^{13}C NMR (δ, 150.9 MHz, $CDCl_3$): 11.3, 11.4, 12.2, 12.3, 13.3, 13.5, 17.7, 19.55, 19.64, 19.7, 19.8, 19.9, 23.5, 23.7, 30.1, 30.8, 31.0, 33.2 (m), 38.7, 39.6, 39.7, 40.3, 40.4, 49.0, 53.1, 93.4, 94.2, 99.2, 99.3, 100.6, 100.7, 101.6, 102.4, 121.3, 121.4, 129.3, 129.5, 129.6, 129.7, 131.3, 133.2, 133.8, 133.9, 134.1, 134.3, 135.0, 135.1, 136.2, 138.0, 144.3, 144.4, 149.4, 153.1, 167.3, 172.1, 174.6, 175.8, 179.3 ppm.

[0280] Ce6-mono-C4^{15} amide, MS-ESI (HRMS) m/z calculated for C38 H46 N5 O5 ($M+H^+$): 652.3493. Found: 652.3491.

[0281] Ce6-bis-C4^{15,17} amide, MS-ESI (HRMS) m/z calculated for C42 H55 N6 O4, ($M+H^+$): 707.4279. Found: 707.4277.

Compound 9-mix (Ce6-mix-$C_{12}^{15,17}$ amide)



1 9-mono 9-bis

[0282] Following general procedure A, compound 1 (0.301 g, 0.486 mmol) and dodecylamine (0.1886 g, 1.018 mmol) and $NaHCO_3$ (0.2054 g, 2.445 mmol) were used. Precipitation of concentrated DCM solution into a cold hexane (in ice bath) and repeated twice to give a mixture 9-mix of compound 9-mono (Ce6-mono-$C12^{15}$ amide) and 9-bis (Ce6-bis-$C12^{15,17}$ amide) as a dark green solid (0.339 g, 82% yield). The products were formed in an approximately 1:1.25 ratio.

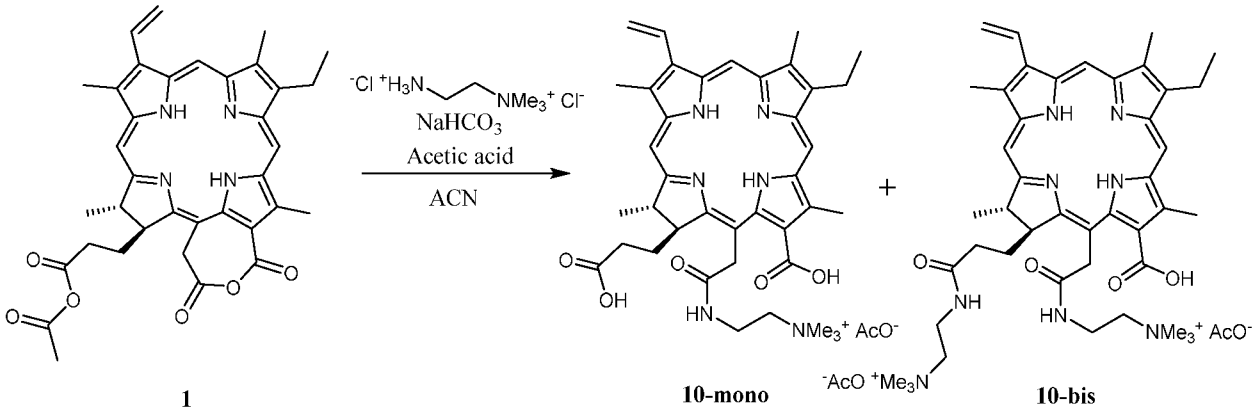
[0283] ^{1}H NMR (δ, 600.13 MHz, $CDCl_3$): -1.82 (brs, 2H), 0.7-0.8 (m, 23H), 0.8-1.2 (m, 25H), 1.2-1.4 (24H), 1.6 (bs, 9H), 2.2, 2.4, 2.8 (bs, 3 x 1H)_3.1-3.3 (m, 9H), 3.40 (m, 5H), 3.58 (m, 5H), 3.69 (m, 5H), 3.43 (bs, 3H), 5.4 (bs, 2H), 6.16 (d, 2H, J=11.6), 6.38 (d, 2H, J=17.8), 7.98 (m, 1H), 8.74 (s, 1H), 9.54 (bs 1H), 9.68 (s, 1H) ppm.

[0284] ^{13}C NMR (δ, 150.9 MHz, $CDCl_3$): 17.7, 19.7, 22.6, 23.3, 23.4, 26.7, 26.8 26.9, 30.0 (complex m), 31.8 (m), 39.5, 39.7, 40.3, 49.2, 53.3, 94.1, 99.0 (x2), 101.8, 121.9, 129.3 (x2), 130.2, 130.4, 135.0, 136.0, 139.3, 144.8, 169.5, 170.1, 172.9, 174.5 ppm.

[0285] Ce6-mono-$C12^{15}$ amide, MS-ESI (HRMS) m/z calculated for C46 H62 N5 O5 ($M+H^+$): 764.4745. Found: 764.4750.

[0286] Ce6-bis-$C12^{15,17}$ amide, MS-ESI (HRMS) m/z calculated for C58 H87 N6 O4, ($M+H^+$): 931.6783. Found: 931.6788.

Compound 10-mix (Ce6-mix-TMEA^{15,17} amide acetate)



[0287] Compound 1 (0.300 g, 0.486 mmol), (2-aminoethyl)trimethylammonium chloride hydrochloride (0.1712 g, 0.978 mmol) and $NaHCO_3$ (0.206 g (2.447 mmol) in CH_3CN anhydrous (20 mL) were used. Acetic acid (1 mL) was added to the reaction mixture, and the reaction mixture was stirred for 30 min. After removal of solvent and volatiles, the residue was washed with DCM (10 mL x 3), combined DCM solution was concentrated, precipitated into diethyl ether, and dried *in vacuo*. 10-mix was obtained as a mixture of compound 10-mono (Ce6-mono-TMEA^{15} amide) and compound 10-bis (Ce6-bis-TMEA^{15,17} amide) as a dark green solid (0.295 g, 90% yield).

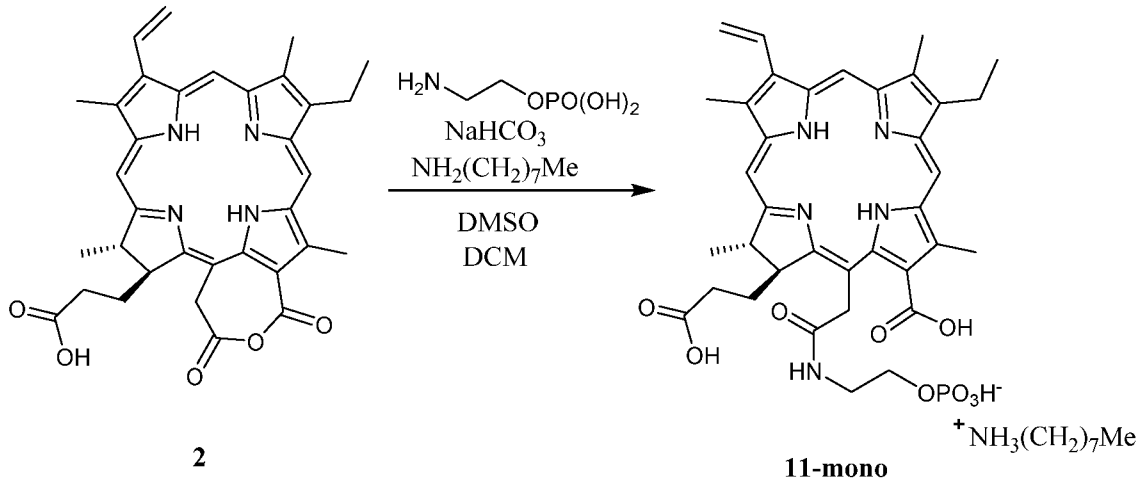
[0288] ^{1}H NMR (δ, 600.13 MHz, $CDCl_3$): -1.52 (br, 2H), 1.53 (m, 5H), 1.77 (m, br, 6H), 2.03 (m, br, 9H), 2.44-2.52 (m, 12H), 2.72 (br, 2H), 3.01-3.55 (m, 15H), 4.29 (m, br, 2H), 6.04 (d, 1H, J=11.6 Hz), 6.23 (d, 1H, J=17.8Hz), 7.97 (m, 1H), 8.21 (m, 1H), 8.21 (br, 1H), 9.48 (br, 1H), 9.54 (br, 1H) ppm.

[0289] ^{13}C NMR (δ, 150.9 MHz, $CDCl_3$): 11.2, 12.0, 12.1, 17.6, 19.5, 22.2, 22.3, 23.3, 23.4, 33.0, 33.9, 38.5, 40.9, 48.6, 48.7, 52.2, 52.7, 52.9, 53.0, 53.6, 63.4, 63.9, 64.6, 98.7, 99.6, 121.4, 129.4, 130.6, 133.4, 133.8, 135.2, 136.2, 137.5, 144.1, 148.9, 152.6, 168.2, 171.7, 174.2, 174.9, 176.0, 178.0 ppm.

[0290] Ce6-mono-TMEA^{15} amide, MS-ESI (HRMS) m/z calculated for C39 H50 N6 O5 (M+H+): 681.3759. Found: 681.3755.

[0291] Ce6-di-TMEA ^{15,17} amide, MS-ESI (HRMS) m/z calculated for C44 H62 N8 O4, (M+H+): 765.4810. Found: 765.4815.

Compound 11-mono (Ce6-mono-EP OA[15])

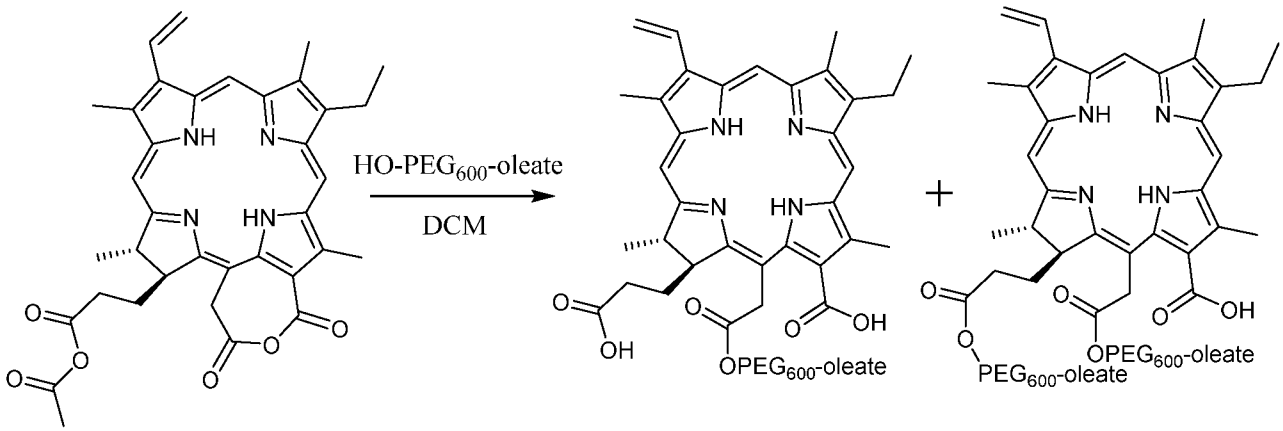


2 11-mono

[0292] 2-Aminoethyl dihydrogen phosphate, 0.186 g (1.29 mmol) and $NaHCO_3$, 0.542 g (6.545 mmol) in DMSO anhydrous (20 mL) was stirred at room temperature for 30 min, the DCM solution of compound 2 (0.400 g, 0.645 mmol in 10 mL DCM) was added dropwise. The mixture was stirred at room temperature for overnight in the absence of ambient light. The reaction mixture was evaporated under vacuum (80ºC, 0.1 mmHg). To the resulting solid was added octylamine in DCM (20 mL) and stirred at room temperature for 30 min. The mixture was filtered, concentrated and precipitated into diethyl ether. Precipitation step was repeated twice, the resulting precipitate was isolated by filtration, washed with diethyl ether (5 mL x 2), then dried *in vacuo*. Compound 11-mono (Ce6-mono-EP[15] amide) was obtained as a dark green solid (0.205 g, 44%).

[0293] MS-ESI (HRMS) m/z calculated for C36 H43 N5 O9 P, (M+H+): 720.2793. Found: 720.2799; (M+Na+): 742.2612. Found: 742.2612. Octylamine ($M+H^+$) was found at m/z 130.1592.

Compound 12-mix (Ce6-mix-PEG$_{600}$-oleate^{15,17} ester)



1 **12-mono** **12-bis**

[0294] To compound 1 (0.501 g, 0.810 mmol) in DCM (20 mL) was added $NaHCO_3$ (2 g, 23.8 mmol) and polyethylene glycol monooleate, MW 860, (1.385 g, 1.610 mmol). After stirring at room temperature in the absence of light overnight, the reaction mixture was filtered, concentrated and precipitated into diethyl ether. The precipitation step was repeated twice, and the combined precipitate was dried *in vacuo*. 12-mix was obtained as a mixture of 12-mono (Ce6-mono-PEG$_{600}^{15}$-oleate ester) and 12-bis (Ce6-bis-PEG$_{600}^{15,17}$-oleate ester) (0.720 g, 80% yield).

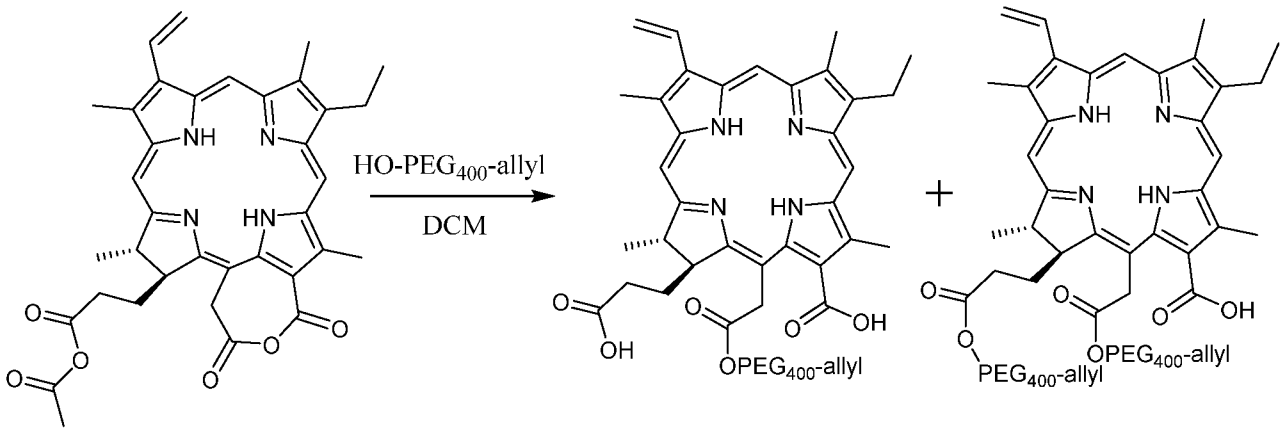
[0295] ^{1}H NMR (δ, 600.13 MHz, $CDCl_3$): -2.3 (bs, 1H), -1.9 (br, 1H), 0.80 (s, 1H), 1.22 (m, 7H), 1.4-1.7 (m, 9H), 1.8-2.3 (m, 7H), 2.3-3.8 (m, 77H), 3.8-4.4 (m, 5H), 5.27 (bs, 1H), 5.4-5.9 (m 2H), 6.01 (d, 2H, J=11.6), 6.24 (d, 2H, J=17.8), 8.00 (m, 1H), 8.70 (m, 1H), 9.56 (s, 2H) ppm.

[0296] ^{13}C NMR (δ, 150.9 MHz, $CDCl_3$): 11.4, 12.2, 14.1, 17.8, 19.7, 22.7, 23.3, 24.9, 27.1, 29.1, 29.5 (many signals), 34.2, 49.0, 63.5, 69 (many signals), 93.7, 98.7, 102.7, 121.0, 125.7, 129.7, 130.1, 133.7, 135.9, 136.2, 143.9, 149.2, 173.8 ppm.

[0297] Ce6-mono-PEG$_{600}^{15}$-oleate ester: MS-ESI m/z, a series of peaks having 6 EO units at ($M+H^+$) m/z 1169.3 as a centered peak with a peak-to-peak mass increment or decrement of 44Da.

[0298] Ce6-di-PEG$_{600}^{15,17}$-oleate ester: MS-ESI m/z, a series of peaks having 6 EO units at ($M+H^+$) m/z 1521.5 as a centered peak with a peak-to-peak mass increment or decrement of 44Da.

Compound 13-mix (Ce6-mix-PEG$_{400}$-allyl^{15,17} ester)



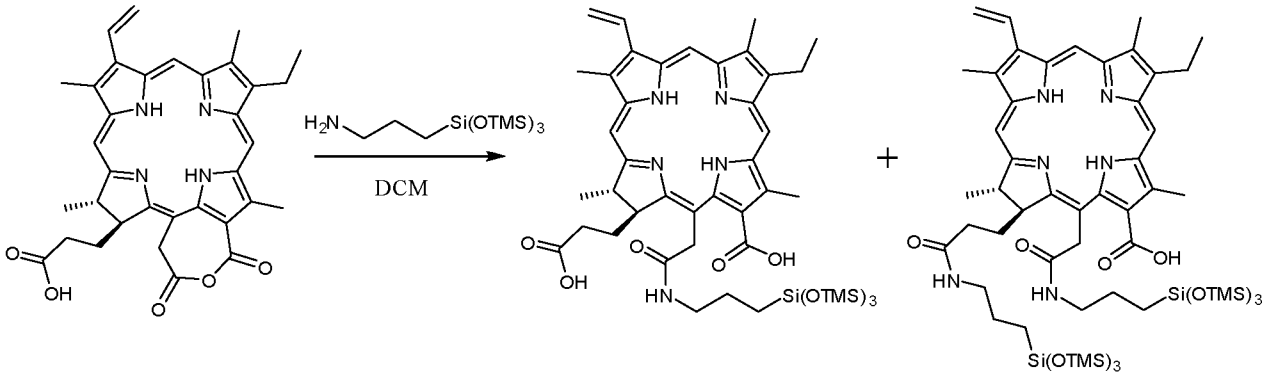
1 **13-mono** **13-bis**

[0299] To compound 1 (0.417 g, 0.672 mmol) in DCM (20 mL) was added $NaHCO_3$ (1.035 g, 11.9 mmol) and polyethylene glycol monoallyl ether, MW 388 based on ^1H NMR, (0.521 g, 1.344 mmol). After stirring at room temperature in the absence of light overnight, the reaction mixture was filtered, concentrated and precipitated into diethyl ether, the precipitation step was repeated twice. The combined precipitate was dried *in vacuo*. 13-mix was obtained as a mixture of 13-mono (Ce6-mono-PEG$_{400}^{15}$-allyl ester) and 13-bis (Ce6-bis-PEG$_{400}^{15,17}$-allyl ester) (0.780 g, 80% yield).

[0300] Ce6-mono-PEG$_{400}^{15}$-allyl ester: MS-ESI m/z, a series of peaks having 8 EO units at ($M+H^+$) m/z 1033.3 as a centered peak with a peak-to-peak mass increment or decrement of 44Da.

[0301] Ce6-bis-PEG$_{400}^{15,17}$-allyl ester: MS-ESI m/z, a series of peaks having 8 EO units at ($M+H^+$) m/z 1161.4 as a centered peak with a peak-to-peak mass increment or decrement of 44Da.

Compound 14-mix (Ce6-mix-T(TMS)SP^{15,17} amide)



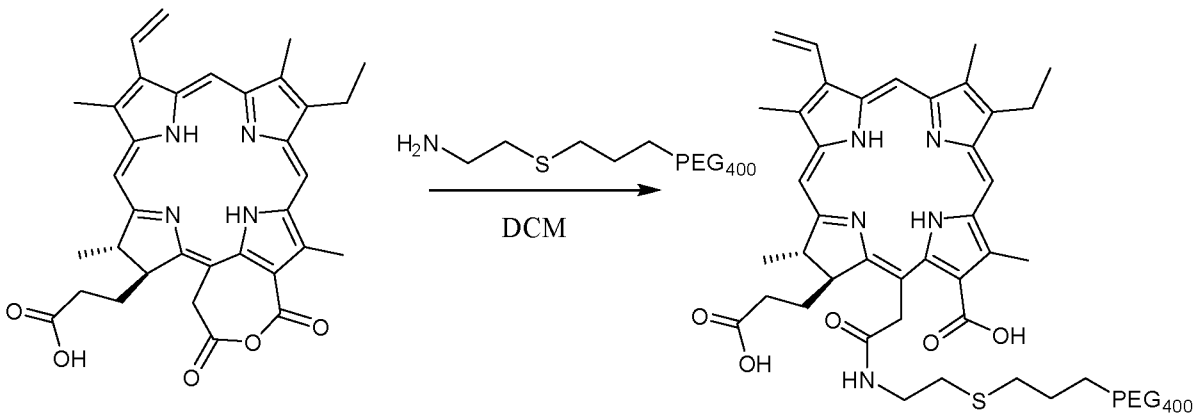
2 14-mono 14-bis

[0302] To compound 1 (0.201 g, 0.323 mmol) in DCM (20 mL) was added (3-aminopropyl)tris(trimethylsiloxy)silane (0.228 g, 0.645 mmol). After stirring at room temperature in the absence of light overnight, solvent and volatiles were removed *in vacuo*, the residue was dissolved in hexane (20 mL), filtered, evaporated and dried *in vacuo*. 14-mix was obtained as a mixture of compound 14-mono (Ce6-mono-T(TMS)SP^{15} amide) and 14-bis (Ce6-bis-T(TMS)SP^{15,17} amide) (0.3081 g, 87% yield).

[0303] Ce6-mono-T(TMS)SP^{15} amide, MS-ESI (HRMS) m/z calculated for C46 H70 N5 O8 Si4 ($M+H^+$): 932.4296. Found: 932.4288.

[0304] Ce6-bis-T(TMS)SP^{15,17} amide, MS-ESI (HRMS) m/z calculated for C58 H103 N6 O10 Si8, ($M+H^+$): 1267.5884. Found: 1267.5876.

Compound 15-mono (Ce6-mono-3TP-PEG$_{400}$^{15} amide)



2 15-mono

[0305] Following general procedure B, compound 2 (0.243 g, 0.420 mmol) and α-hydroxy-poly(ethylene glycol)-ω-(ethylthio)ethylamine (0.195 g, 0.420 mmol) were used. Ce6-mono-3TP-PEG_{400}^{15} amide was obtained as a dark green solid (0.394 g, 90% yield).

[0306] MS-ESI m/z, a series of peaks having 8 EO units at ($M+H^+$) m/z 1066.6 as a centered peak with a peak-to-peak mass increment or decrement 44Da.

General procedure C – synthesis of Ce6-Copper complexes

[0307] The Ce6 compound (1 eq.) prepared from general procedure A or B was solubilized in a solvent mixture of dichloromethane and methanol at 1:2 ratio. Copper (II) acetate (1.2 eq) was added and the reaction mixture was heated at 45°C under N_2 in the absence of ambient light for 2 h. The solvents were removed under reduced pressure. The residue was extracted with DCM (10 mL x 3). The combined DCM extracts were concentrated, precipitated from ethyl acetate and dried *in vacuo*.

Compound Cu Ce6-mix-$DMAE^{15,17}$ amide

[0308] Following general procedure C, Ce6-mix-$DMAE^{15,17}$ amide (0.102 g, 0.151 mmol) and $Cu(OAc)_2$ (0.033 g, 0.181 mmol) were used. Cu Ce6-mix-$DMAE^{15,17}$ amide was obtained as a mixture of Cu Ce6-mono-$DMAE^{15}$ amide and Cu Ce6-bis-$DMAE^{15,17}$ amide, as a green solid (0.1273 g, 95% yield).

[0309] Cu Ce6-mono-$DMAE^{15}$ amide: MS-ESI (HRMS) m/z calculated for C38 H45 Cu N6 O5 ($M+H^+$): 728.2742. Found: 728.2705.

[0310] Cu Ce6-bis-$DMAE^{15,17}$ amide: MS-ESI (HRMS) m/z calculated for C42 H55 Cu N8 O4 ($M+H^+$): 798.3637. Found: 798.3648.

Compound Cu Ce6-mix-$C4^{15,17}$ amide

[0311] Following general procedure C, Ce6-mix-$C4^{15,17}$ amide (0.100 g, 0.153 mmol) and $Cu(OAc)_2$ (0.034 g, 0.184 mmol) were used. Cu Ce6-mix-$C4^{15,17}$ amide was obtained as a mixture of Cu Ce6-mono-$C4^{15}$ amide and Cu Ce6-bis-$C4^{15,17}$ amide, as a green solid (0.114 g, 89% yield).

[0312] Cu Ce6-mono-$C4^{15}$ amide: MS-ESI (HRMS) m/z calculated for C38 H44 Cu N5 O5 ($M+H^+$): 713.2638. Found: 713.2625.

[0313] Cu Ce6-bis-$C4^{15,17}$ amide: MS-ESI (HRMS) m/z calculated for C42 H53 Cu N6 O4 ($M+H^+$): 768.3419. Found: 768.3416.

Compound Cu Ce6-mix-$C12^{15,17}$ amide

[0314] Following the general procedure C, Ce6-mix-$C12^{15,17}$ amide (0.101 g, 0.130 mmol) and $Cu(OAc)_2$ (0.029 g, 0.156 mmol) were used. Cu Ce6-mix-$C12^{15,17}$ amide was obtained as a mixture of Cu Ce6-mono-$C12^{15}$ amide and Cu Ce6-bis-$C12^{15,17}$ amide, as a green solid (0.108 g, 86% yield).

[0315] Cu Ce6-mono-$C12^{15}$ amide: MS-ESI (HRMS) m/z calculated for C46 H60 Cu N5 O5 ($M+H^+$): 825.3885. Found: 825.3866.

[0316] Cu Ce6-bis-$C12^{15,17}$ amide: MS-ESI (HRMS) m/z calculated for C58 H85 Cu N6 O4 ($M+H^+$): 992.5923. Found: 992.5926.

Compound Cu Ce6-mono-$DMAE^{15}$ amide

[0317] Following the general procedure C, Ce6-mono-$DMAE^{15}$ amide (0.207 g, 0.311 mmol) and $Cu(OAc)_2$ (0.069 g, 0.373 mmol) were used. Cu Ce6-mono-$DMAE^{15}$ amide was obtained as a green solid (0.253 g, 92% yield).

[0318] Cu Ce6-mono-$DMAE^{15}$ amide: MS-ESI (HRMS) m/z calculated for C38 H45 Cu N6 O5 ($M+H^+$): 728.2742. Found: 728.2690.

Compound Cu Ce6-mono-$DEAEAE^{15}$ amide

[0319] Following the general procedure C, Ce6-mono-$DEAEAE^{15}$ amide (0.220 g, 0.298 mmol) and $Cu(OAc)_2$ (0.067 g, 0.358 mmol) were used. Cu Ce6-mono-$DEAEAE^{15}$ amide was obtained as a green solid (0.257 g, 90% yield).

[0320] Cu Ce6-mono-$DEAEAE^{15}$ amide: MS-ESI (HRMS) m/z calculated for C42 H54 Cu N7 O5 ($M+H^+$): 799.3477. Found: 799.3440.

Compound Cu Ce6-mix-$BAE^{15,17}$ amide

[0321] Following general procedure C, Ce6-mix-$BAE^{15,17}$ amide (0.136 g, 0.196 mmol) and $Cu(OAc)_2$ (0.044 g, 0.235 mmol) were used. Cu Ce6-mix-$BAE^{15,17}$ amide was obtained as a

mixture of Cu Ce6-mono-BAE^{15} amide and Cu Ce6-bis-BAE^{15,17} amide, as a green solid (0.146 g, 84% yield).

[0322] Cu Ce6-mono-BAE^{15} amide: MS-ESI (HRMS) m/z calculated for C40 H49 Cu N6 O5 ($M+H^+$): 756.3055. Found: 756.3056.

[0323] Cu Ce6-bis-BAE^{15,17} amide: MS-ESI (HRMS) m/z calculated for C42 H55 Cu N8 O4 ($M+H^+$): 854.4268. Found: 854.4269.

Compound Cu Ce6-mix-TMEA^{15,17} amide acetate salt

[0324] Following general procedure C, Ce6-mix-TMEA^{15,17} amide (0.102 g, 0.138 mmol) and $Cu(OAc)_2$ (0.031 g, 0.171 mmol) were used. CuCe6-mix-TMEA^{15,17} amide acetate salt was obtained as a mixture of Cu Ce6-mono-TMEA^{15} amide and Cu Ce6-bis-TMEA^{15,17} amide, as a dark green solid (0.117 g, 88% yield).

[0325] Cu Ce6-mono-TMEA^{15} amide: MS-ESI (HRMS) m/z calculated for C39 H47 Cu N6 O5 ($M+H^+$): 742.2898. Found: 742.2878.

[0326] Cu Ce6-bis-TMEA^{15,17} amide: MS-ESI (HRMS) m/z calculated for C44 H59 Cu N8 O4 (M-H+): 826.3955. Found: 826.3960. ($M+H2^+$): 413.7017. Found: 413.7019.

Compound Cu Ce6-mix-DMAB^{15,17} amide

[0327] Following general procedure C, Ce6-mix- DMAB^{15,17} amide (0.105 g, 0.152 mmol) and $Cu(OAc)_2$ (0.0340 g, 0.187 mmol) were used. Cu Ce6-mix-DMAB^{15,17} amide was obtained as a mixture of Cu Ce6-mono-DMAB^{15} amide and Cu Ce6-bis-DMAB^{15,17} amide, as a green solid (0.105 g, 79% yield).

[0328] Cu Ce6-mono-DMAB^{15} amide: MS-ESI (HRMS) m/z calculated for C40 H49 Cu N6 O5 ($M+H^+$): 756.3055. Found: 756.3040.

[0329] Cu Ce6-di-DMAB^{15,17} amide: MS-ESI (HRMS) m/z calculated for C46 H63 Cu N8 O4 ($M+H^+$): 854.4263. Found: 854.4254.

Compound Cu Ce6-mono-3TP-PEG_{400}^{15} amide

[0330] Following general procedure C, Ce6-mono-3TP-PEG_{400}^{15} amide (0.702 g, 0.657 mmol) and $Cu(OAc)_2$ (0.184 g, 0.986 mmol) were used. Cu Ce6-mono-3TP-PEG_{400}^{15} amide was obtained as dark blue green solid (0.529 g, 72% yield).

[0331] Cu Ce6- mono-3TP-PEG_{400}^{15} amide: MS-ESI (HRMS) m/z calculated for C55 H78 Cu N5 O14 S (EO units n=8) ($M+H^+$): 1127.4557. Found: 1127.4585.

Compound Zn Ce6-mix-$DMAE^{15,17}$ amide

[0332] The mixture of Ce6-mix-$DMAE^{15,17}$ amide (0.903 g, 1.295 mmol) and Zine acetate (0.364 g, 1.943 mmol) in MeOH (20 mL) was heated at 60° C under N_2 in dark for 3 hours, the solvents were removed under reduced pressure. The residue was extracted with DCM, 10 mL 3 times. The combined DCM extracts were concentrated and precipitated from ethyl acetate/ether (1:1) and repeated twice to give Zn Ce6-mix-$DMAE^{15,17}$ amide as dark blue solid (0.688 g, 70% yield).

[0333] ^1H NMR (δ, 500.25 MHz, d_6-DMSO): 1.64-1.72 (m, 6H), 1.85 (m, 9H), 2.35 (s, br, 5H), 2.60 ((s, br. 2H), 2.76 (m, br, 3H), 3.33-3.35 (m, 6H), 3.38 (m, 3H), 3.45 (m, 2H), 3.82 (m, 3H), 4.37-4.55 (m, 2H), 6.00 (m, 1H), 6.23 (m, 1H), 8.24 (m, 1H), 8.8.62-8.75 (m, 1H), 9.45 (m, 1H), 9.54 (m, 1H) ppm.

[0334] Zn Ce6-mono-$DMAE^{15}$ amide: MS-ESI (HRMS) m/z calculated for C38 H45 N6 O5 Zn ($M+H^+$): 729.2737. Found: 729.2714.

[0335] Zn Ce6-di-$DMAE^{15,17}$ amide: MS-ESI (HRMS) m/z calculated for C42 H55 N8 O4 Zn ($M+H^+$): 799.3632. Found: 799.3618.

Compound Zn Ce6-mono-3TP-PEG_{400}^{15} amide

[0336] The mixture of Ce6-mono-3TP-PEG_{400}^{15} amide (0.501 g, 0.469 mmol) and Zine acetate (0.129 g, 0.704 mmol) in MeOH (20 mL) was heated at 60° C under N_2 in dark for 3 hours, the solvents were removed under reduced pressure. The residue was extracted with DCM, 10 mL 3 times. The combined DCM extracts were concentrated and precipitated from ethyl acetate/ether (1:3) and repeated twice, dried under vacuum to give Zn Ce6- mono-3TP-PEG_{400}^{15} amide as dark blue solid (0.489 g, 92% yield).

[0337] Zn Ce6-mono-3TP-PEG_{400}^{15} amide: MS-ESI (HRMS) m/z calculated for C55 H78 N5 O14 S Zn (EO units n=8) ($M+H^+$): 1128.4552. Found: 1128.4573.

Compound Pd Ce6-mix-$DMAE^{15,17}$ amide

[0338] The mixture of Ce6-mix-$DMAE^{15,17}$ amide (0.8002 g, 1.151 mmol) and palladium (II) acetate (0.3879 g, 1.727 mmol) in a solvent mixture of THF (20 mL) and MeOH (20 mL) was heated at 60º C under N_2 in dark for 20 hours, the solvents were removed under reduced pressure. The residue was extracted with DCM, 20 mL 3 times. The combined DCM extracts were concentrated and precipitated from ethyl acetate/ether (1:1) and repeated twice, dried under vacuum to give Pd Ce6-mix-$DMAE^{15,17}$ amide as dark blue-green solid (0.515 g, 56% yield).

[0339] Pd Ce6-mono-$DMAE^{15}$ amide: MS-ESI (HRMS) m/z calculated for C38 H45 N6 O5 Pd ($M+H^+$): 771.2486. Found: 771.2493.

[0340] Pd Ce6-di-$DMAE^{15,17}$ amide: MS-ESI (HRMS) m/z calculated for C42 H55 N8 O4 Pd ($M+H^+$): 841.3381. Found: 841.3362.

Biological activity

Example 1

[0341] *E. Amylovora* were grown in liquid medium. Samples were incubated for 5 min or 30 min with between 1 µM to 100 µM photosensitizer Ce6-mix-$DMAE^{15,17}$ amide (PS), and then illuminated with 395 nm (14.8mW/cm^2) for 30 min. Colony forming units (CFU) of the bacteria were counted on the plates. The results are summarized on Figure 1.

[0342] *Caption for Figure 1:* Relative inactivation of Erwinia amylovora gram-negative bacteria using Ce6-mix-$DMAE^{15,17}$ amide (PS). Samples were incubated for either 5 min or 30 min and subsequently irradiated with 395 nm light (14.8 mW/cm^2) for 30 min. Data represents mean ± standard deviation ($n \geqslant 3$ replicates).

Example 2

[0343] *Xanthomonas axonopodis* were grown in liquid medium. Samples were incubated with 1 µM to 100 µM photosensitizer Ce6-mix-$DMAE^{15,17}$ amide (PS) for 5 min or 10 min, and then

illuminated with 395 nm (14.8mW/cm2) for 30 min or 5 min. Colony forming units (CFU) of the bacteria were counted on the plates. The results are summarized on Figure 2.

[0344] *Caption for Figure 2:* Relative inactivation of *Xanthomonas axonopodis* gram-negative bacteria using Ce6-mix-DMAE^{15,17} amide (PS). Samples were incubated for either 5 min or 30 min and subsequently irradiated with 14.8mW/cm^2 light at 395nm for 30 min. Data represents mean ± standard deviation (n = 4 replicates).

Example 3

[0345] *R. fascians* was cultivated in DSMZ 53 medium, with supplemented glucose. Bacterial suspension was cultivated in 20 mL of bacterial suspension in 100 mL glass flasks in a shaking incubator at 26°C for two days. Samples were incubated with 1 µM to 100 µM photosensitizer Ce6-mix-DMAE^{15,17} amide (PS) for 5 min or 10 min, and then illuminated with 395 nm (14.8mW/cm^2) for 30 min or 5 min. Colony forming units (CFU) of the bacteria were counted on the plates at 120 h post illumination. The results are summarized on Figure 3.

[0346] *Caption for Figure 3:* Relative inactivation of *Rhodococcus fascians* gram-positive bacteria using Ce6-mix-DMAE^{15,17} amide (PS). Samples were incubated for either 5 min or 30 min and subsequently irradiated with 14.8mW/cm^2 light at 395 nm for 30 min. Data represents mean ± standard deviation (n = 3 replicates).

Example 4

[0347] Comparative dose response for Ce6-mix-DMAE^{15,17} amide and Ce6Na3 under light conditions in *Pseudomonas syringae pv. tabacii.* samples were obtained. The *Pseudomonas syringae pv. tabacii.* samples were incubated, with the respective photosensitizer, on a shaking incubator for 30 min and then subjected to 1000 µmol/m^2/s photosynthetically active radiation for 1 h. The results are summarized on Figure 4.

Example 5

[0348] *Alternaria solani* mycelia were grown in liquid medium for 24 h. Small spheres of the mycelia (average diameter 2mm) were incubated for 100 min with 1 µM to 100 µM Ce6-mix-DMAE^{15,17} amide. Samples were illuminated with 395 nm (14.8mW/cm2) for 120 min and the radial growth of mycelial patches after 7 d on agar medium was measured. A sample was considered dead if there was no growth observable after 7 d on agar plates. The results are summarized in Table 1:

Table 1. Effect of Ce6-mix-DMAE^{15,17} amide (PS) against *Alternaria solani*

	Percentage of dead samples [%]	Sample size (n)
0 µM PS no light	0	23
100 µM PS no light	0	13
0 µM PS + light	0	24
1 µM PS + light	0	15
10 µM PS + light	100	15
100 µM PS + light	100	15

Example 6

[0349] *Botrytis cinerea* mycelia were grown in liquid medium for 48 h. Small spheres of the mycelia (average diameter 2 mm) were incubated for 100 min with 1 µM to 100 µM Ce6-mix-DMAE^{15,17} amide. Samples were illuminated with 395 nm (14.8mW/cm^2) for 120 min and the radial growth of mycelial patches after 7 d on agar medium was measured. A sample was considered dead if there was no growth observable after 7 d on agar plates. The results are summarized in Table 2:

Table 2. Effect of Ce6-mix-DMAE^{15,17} amide (PS) against *Botrytis cinerea*

	Percentage of dead samples [%]	Sample size (n)
0 µM PS no light	0	9
100 µM PS no light	33.33	6
0 µM PS + light	0	9
1 µM PS + light	0	6
10 µM PS + light	50	6
100 µM PS + light	100	6

Example 7

[0350] Control of dollar spot fungus (*Sclerotinia homoeocarpa*) with Ce6-mix-DMAE^{15,17} amide and Ce6Na3 (comparative) was assessed. Treatments were amended into Potato Dextrose Agar (PDA) at desired concentrations. Then, a 5 mm diameter plug of a *Sclerotinia homoeocarpa* isolate (3 isolates total tested) was inoculated into the center of the amended Petri-dish and incubated at 21°C in the dark for 24 h. After 24 h, one set of Petri-dishes (in triplicate) was left in the dark (no light) and one set was placed under illumination (light) for the remainder of the experiment (all at 21°C). Radial growth of the fungus was monitored daily until the growth of *S. homoeocarpa* on non-amended PDA reached the edge of the Petri-

dish. Illumination was provided by fluorescent lights emitting about 180 µmol/m^2/s photosynthetically active radiation (PAR). The results are summarized in Table 3:

Table 3. Comparative dose response for Ce6-mix-DMAE^{15,17} amide and Ce6Na3 under light and dark conditions in *Sclerotinia homeocarpa* agar plate assay.

	Inhibition, %	
	Ce6Na3	Ce6-mix-DMAE^{15,17} amide
	Light	
5 µM	39	95
10 µM	74	93
31 µM	99	100
5 µM	13	4
10 µM	26	38
31 µM	44	55

Example 8

[0351] Control of the fungal plant pathogen *Colletotrichum orbiculare* ATC20767 *(*Cgm*)* on the host plant *Nicotiana benthamiana* following treatment with Ce6-mix-DMAE^{15,17} amide combined with a surfactant was assessed. Treatments were applied to *N. benthamiana* plants approximately 2 h prior to inoculation with a spore suspension of Cgm. Plants were then exposed to light for a 24-hour period followed by dark incubation until disease symptoms were evident on the water treated control plants. Once disease symptoms were evident, lesions were counted and leaf area measured in order to determine the number of lesions/cm^2 leaf area. Four replicate plants were used per treatment and plants were randomized under the light source. Illumination was provided by LED lights emitting about 180 µmol/m^2/s photosynthetically active radiation (PAR). The results are shown on Figure 5.

[0352] *Caption for Figure 5:* Inhibition of *Colletotrichum orbiculare* ATC20767 fungus lesion formation on *Nicotiana benthamiana* host plant. Ce6-mix-DMAE^{15,17} amide was applied 2 h before inoculation with fungal spores followed by a 24-h light period.

Example 9

[0353] To evaluate the effect of Ce6-mix-DMAE^{15,17} amide on insect pests, the product was applied on Poinsettia plants that were infested with whiteflies (silverleaf whitefly *Benmisia tabaci*) and compared with untreated control. For each treatment, five single plant replicates

were arranged in a RCB design in a greenhouse setting. Plants were placed on wire mesh benches. Treatments were applied using a CO2 powered backpack sprayer with a single solid cone nozzle (TG1) at 60 psi. During the application all plants were treated individually then placed outdoors into direct sunlight for 8hrs before returning to the greenhouse plot area. A second application was made 7 days after the first application.

[0354] Two discs (d=5.47cm2) were taken from each plant/plot and were viewed under a stereoscope. nymphs of whiteflies were counted on both discs 1 day before application, and 6, 13, 20 and 28 days after application (DAA). Upon initiation of the trial, the whitefly population was considered uniform across all plant/plots with an average of 48 nymphs/sample. The whitefly populations after application are summarized in Table 4A. Ce6-mix-DMAE^{15,17} amide reduced the number of whitefly nymphs in comparison with untreated control.

[0355] Phytotoxicity of the plants was rated (0-10, where 0 = healthy plant, 10 = dead plant) at 6 DAA and 13 DAA, by visual observations for symptoms such as chlorosis, necrosis, deformation, stunting and compared to plants in the untreated control. The results are summarized in Table 4B. Ce6-mix-DMAE^{15,17} amide treatment did not cause phytotoxicity on the plants.

Table 4A. Number of live nymphs of whiteflies per sample before and after treatment with Ce6-mix-DMAE^{15,17} amide.

Treatment	Average number of live nymphs of whiteflies/sample				
	-1 DAA	6 DAA	13DAA	20DAA	28 DAA
0.02 wt% Ce6-mix-DMAE^{15,17} amide + 99.98 wt% water	96.8	57.5	52.1	53	30.9
Untreated Control	93	72	90.12	81.6	69.2

Table 4B. Phytotoxicity of poinsettia plants after treatments.

Treatment	Phytotoxicity (0-10)	
	6 DAA	13DAA
0.02 wt% Ce6-mix-DMAE^{15,17} amide + 99.98 wt% water	0	0
Untreated Control	0	0

Example 10

[0356] Experiments were conducted to evaluate anti-fungal activity of several Ce6 derivatives synthesized herein. The following methods were used, and the results are summarized in Tables 5 and 6.

[0357] Agar protocol: control of dollar spot fungus (*Sclerotinia homoeocarpa*) with modified Ce6 was assessed. Treatments were amended into Potato Dextrose Agar (PDA) at desired concentrations. Then, a 5mm diameter plug of a *Sclerotinia homoeocarpa* isolate (3 isolates total tested) was inoculated into the center of the amended Petri-dish and incubated at 21°C in the dark for 24 hours. After 24 hours, one set of Petri-dishes (in triplicate) was left in the dark and one set was placed under illumination for the remainder of the experiment (all at 21°C). Radial growth of the fungus was monitored daily until the growth of *S. homoeocarpa* on non-amended PDA reaches the edge of the Petri-dish. Illumination was provided by fluorescent lights emitting about 180 µmol/m2/s photosynthetically active radiation (PAR).

[0358] Broth protocol: control of dollar spot fungus (*Sclerotinia homoeocarpa*) with modified chlorins was assessed. Treatments were prepared in Phosphate Buffered Saline (PBS) in 24 well plates (in duplicates for light vs. dark incubation) at desired concentrations. Then, a 5mm diameter plug of a *Sclerotinia homoeocarpa* isolate (3 isolates total tested) was inoculated into the PBS and incubated at 21°C in the dark for 2 hours. After 2 hours, one of the 24 well plates (with isolates in triplicate) was left in the dark and one 24 well plate was placed under illumination for 1 hour (all at 21°C). Following illumination, fungal plugs were removed from PBS, blotted dry on sterile filter paper and transferred to non-amended Potato Dextrose Agar (PDA). Radial growth of the fungus was monitored daily until the growth of *S. homoeocarpa* reached the edge of the Petri-dish. Illumination was provided by LED lights emitting about 1000 µmol/m2/s photosynthetically active radiation (PAR).

Table 5. Effect of Ce6 derivatives on dollar spot fungus

Agar data	Inhibition, % 10uM	
	Dark	Light
Ce6 Na_3	26	74
Ce6-mix-DEAEAE[15,17] amide	15	100
Ce6-mono-BAE[15] amide	49	99

Table 6. Effect of Ce6 derivatives on dollar spot fungus

Broth data	Inhibition, %			
	10uM		100uM	
	Dark	Light	Dark	Light
Ce6Na3	-4	53	16	66
Ce6-mix-DMAB[15,17] amide	3	58	—	—
Ce6-mono-EP OA[15]	—	—	-5	71
Ce6-C4	13	86	—	—
Ce6-T(TMS)SP[15,17] amide	1	60	—	—
Ce6-mix-PEG_{400}[15,17] allyl ester	—	—	13	96
Ce6-mix-PEG_{600}[15,17] oleate ester	—	—	26	92

Example 11

[0359] Experiments were conducted to evaluate control of the gram-negative bacterial plant pathogen *Pseudomonas syringae* pv. *tabaci* with modified Ce6. Treatments were prepared in Phosphate Buffered Saline (PBS) in 96 well plates at desired concentrations. A bacterial suspension was inoculated into the PBS and incubated at 28°C in the dark for 30 min. After 30 min, the 96 well plate was placed under illumination for 1 hour (at 21°C). A separate plate prepared at the same time was kept in the dark without illumination and served as dark control. Following illumination, bacterial suspensions were serially diluted and 10 µL of each dilution was spread uniformly on Tryptic Soy Agar (TSA) plates and placed in the dark in an incubator at 28°C for 48 hours. After 48 hours, bacterial colonies were counted and results were log transformed (log colony forming units (CFU)/mL). The relative inactivation was determined by taking the difference between logCFU(PBS control) and logCFU (treatments). Sample Illumination was provided by LED lights (Heliospectra RX30) emitting about 1000 µmol/m^2/s photosynthetically active radiation (PAR).

[0360] The modified Ce6 that were evaluated are the Ce6-mix-DMAE[15,17] amide, Ce6-bis-DMAE[15,17] amide and Ce6-mono-DMAE[15] amide. The results are presented in Table 7.

Table 7. Effect of Ce6 derivatives on dollar spot fungus

Treatments	Relative Inactivation ($log[CFU_{control}\ mL^{-1}] - log[CFU_{treatment}\ mL^{-1}]$)	
	Light	Dark
Ce6Na3	0.39 ± 0.29	-0.03 ± 0.13
Ce6-mix-DMAE[15,17] amide	7.98 ± 0.65	0.76 ± 0.24
Ce6-bis-DMAE[15,17] amide	7.98 ± 0.65	1.13 ± 0.42

Ce6-mono-DMAE^{15} amide	7.98 ± 0.65	0.21 ± 0.33

[0361] It can be seen that all forms of Ce6 DMAE amide can be used (i.e., Ce6-mix-DMAE^{15,17} amide, Ce6-bis-DMAE^{15,17} amide or Ce6-mono-DMAE^{15} amide), with the relative inactivation obtained being the same. This is due to the data being represented as relative inactivation (i.e. log ratio between PBS control and treatment). Since, with all forms of Ce6 DMAE amide, the treatments killed all bacteria leaving no colony forming units, the value was set to 1 CFU/mL so as to not generate a mathematical error. The degree of inactivation is therefore dependent on the control counts and hence the values between the treatments are the same. These experiments nonetheless show that all forms of Ce6 DMAE amide are active against gram-negative bacteria.

Example 12

Effect of treatments on strawberry plants (Fragaria x ananassa) tolerance to salt stress

[0362] In this example, the effects of modified chlorin compounds were tested on strawberry plants (Fragaria x ananassa) cv Delizz. The experiments were carried out in a greenhouse. Tests were designed to determine the activity of compounds on strawberry plants tolerance to salt stress.

[0363] In the experiments, seedlings of strawberry plants were grown in 5-inch plastic pots filled with professional soil mix (LC 1 Sunshine, Sungro Horticulture, Canada) and irrigated with fertilized water on a regular basis. The strawberry plants at 4-5 leaf stage were treated with 3 foliar applications of different formulations using hand hold Spray bottle and providing an even coverage. The plants were sprayed with 7 days interval. Twenty-four hours after the first spray, the plants were exposed to salinity stress by soaking plant roots in 15 mM sodium chloride solution. The salinity level was gradually increased to 20 mM NaCl and salt soaking was applied on a 5 to 7 days interval schedule. Plants were harvested 3 weeks after last foliar spray. Surfactant was added to each treatment. The experiment was set out in a completely randomized design with 5 replications for each treatment.

Table 8: Effect of treatments on strawberry plants (Fragaria x ananassa) tolerance to salt stress.

#	Treatment	Above-ground fresh biomass, % Increase

1	Salt Control	0
2	0.05% Cu-Ce_6-mix-$DMAE^{15,17}$ amide+ 0.05% surfactant	12
3	0.05% Ce_6-mono-3TP-PEG_{400}^{15} amide + 0.05% surfactant	22
4	0.05% Cu-Ce_6-mono-3TP-PEG_{400}^{15} amide + 0.05% surfactant	11

[0364] Strawberry plants treated with tested chlorin compounds enhanced plants tolerance to salinity stress.

Example 13

Effect of treatments on strawberry plants (Fragaria x ananassa) tolerance to drought stress

[0365] In this example, the effects of modified chlorin compounds were tested on strawberry plants (Fragaria x ananassa) cv Delizz. The experiments were carried out in a greenhouse. Tests were designed to determine the activity of compounds on strawberry plants tolerance to drought stress.

[0366] In the experiments, seedlings of strawberry plants were grown in 5-inch plastic pots filled with professional soil mix (LC 1 Sunshine, Sungro horticulture, Canada) and irrigated with fertilized water on a regular basis. Strawberry plants at 4-5 leaf stage were treated with 3 foliar applications of different Suncor formulations using hand hold Spray bottle and providing an even coverage. The plants were sprayed with 7 days interval. After first foliar treatment and during the experiment duration, strawberry plants were exposed to reduced water regime (drought stress) until the wilting point (20 to 30% soil moisture capacity - SMC) and watered up to 50% SMC. Plants were harvested 3 weeks after the last foliar spray. Surfactant was added to each treatment. The experiment was set out in a completely randomized design with seven replications for each treatment.

Table 9: Effect of treatments on strawberry plants tolerance to drought stress

#	Treatment	Above-ground fresh biomass, % increase

1	Drought Control	0
2	0.05% Ce_6-mix-$DMAE^{15,17}$ amide + 0.05% surfactant	12
3	0.05% Cu-Ce_6-mix-$DMAE^{15,17}$ amide + 0.05% surfactant	26
4	0.05% Ce6-mono-3TP-PEG_{400}^{15} amide+ 0.05% surfactant	12
5	0.05% Cu-Ce6-mono-3TP-PEG_{400}^{15} amide + 0.05% surfactant	14
6	0.05% surfactant	4

[0367] Strawberry plants treated with tested chlorin compounds enhanced plants tolerance to drought stress.

Example 14

Effect of treatments on tomato plants (*Solanum lycopersicum*) cv. Tiny Tim tolerance to heat stress

[0368] The experiments were carried out in a Growth Chamber in controllable conditions. Tests were designed to determine the activity of compounds on tomato plants tolerance to heat stress.

[0369] In the experiments, tomato plants cv. Tiny Tim were grown in the greenhouse at the temperature 24-26^{0}C. Tomato seedlings were transplanted into 5" plastic pots containing industrial soil mix (LC 1 Sunshine, Sungro Horticulture, Canada). At 5 to 6 leaves stage, plants were treated (foliar spray to run-off) with tested solutions using hand hold Spray bottle and providing an even coverage. Forty-eight hours after spray plants were moved into the Growth Chamber and exposed to heat stress for 10 days. Tomato plants were regularly watered to avoid water deficiency. Ten days later, tomato plants were transferred back to the greenhouse and treated with tested solutions for a second time. Forty-eight hours after second spray plants were placed to the Growth chamber and exposed to heat stress for another 10 days. Growth Chamber conditions: 16 h/8 h light/dark photoperiod; temperature during the dark 19^{o}C; temperatures during the light period – 4 h gradual increase in temperature from 19^{0}C to 37^{0}C, 8 h - 37^{0}C, gradual decrease in temperature to 19^{0}C. Foliar treatments (spays) were applied 2 times. Surfactant was added to each treatment. The

experiment was set out in a completely randomized design with six replications for each treatment.

Table 10: Effect of chlorin formulations on tomato plants tolerance to heat stress.

#	Treatment	Above ground fresh biomass, % increase
1	Heat Control	0
2	0.05% Cu-Ce_6-mix-$DMAE^{15,17}$ amide + 0.05% surfactant	11
3	0.05% Ce_6-mono-3TP-PEG_{400}^{15} amide+ 0.05% surfactant	10
4	0.05% Cu-Ce_6-mono-3TP-PEG_{400}^{15} amide + 0.05% surfactant	10
5	0.05% surfactant	3

[0370] Novel chlorin formulations enhanced tomato plants tolerance to heat stress and increased plants biomass in comparison with untreated Control.

Example 1

Effect of treatments on Kentucky Bluegrass (*Poa pratensis*) tolerance to salt stress

[0371] Kentucky bluegrass (Poa pratensis) was grown under greenhouse conditions for ~3 weeks. After 3 weeks, plants were sprayed with formulations and allowed to sit for 24 hours, after which the pots were placed in a 170 mM NaCl solution until the soil was saturated. The salt application was repeated again 7 days later for a total of 2 salt applications. Salinity stress was evaluated based on a turf quality scale of 1 – 9; where 1 = dead, brown turf; 6 = minimally acceptable turf quality (based on standards for golf courses or sports fields); and 9 = dense, dark green turf (healthy). Data are average of 5 replicates.

Table 11: Effect of salt stress on turf quality

Treatment	Turf Quality
0.1% Ce_6Na_3	6
0.1% Zn-Ce_6-mix-$DMAE^{15,17}$ amide	5.8
0.1% Cu-Ce_6-mix-$DMAE^{15,17}$ amide	6

0.1% Cu-Ce_6-mono-3TP-PEG_{400}^{15} amide	6.2
Untreated control	5

Example 16

Effect of treatments on silkworms

[0372] Experiments were conducted to evaluate the toxicity of a photosensitizer compounds to silkworms *Bombyx mori* (L.) larvae.

[0373] Colony of Silkworms (*Bombyx mori*) third instar larvae was purchased from the distributor Recorp Inc. (Ontario, Canada) and was maintained on fresh mulberry leaves (*Morus rubra*) for 2 days before the treatment.

[0374] Mulberry shoots were harvested from a tree grown outside and had not been treated with any pesticides. Fresh mulberry shoots were washed in tap water and then air-dried.

[0375] Small mulberry shoots (8-10 leaves) were excised from the mature healthy brunch and inserted into water-filled 50 ml plastic vials. The vials were covered with the lead and plastic mesh to prevent water evaporation and larvae drowning. Host plant cuttings were sprayed with tested solutions until run-off and vials with sprayed shoots were placed into 1L transparent plastic containers lined with a filter paper.

[0376] Homogenous silkworm larvae (3^{rd} instar) were sprayed separately and released on treated mulberry shoots into containers. Soft fine paintbrush was used to handle the insects. Containers with plant shoots and insects were covered with white mesh leads.

[0377] All treatments were applied as a fine spray using a 2 oz hand-held mist sprayer-bottle (ULINE, Canada). Water treatment was used as a Control.

[0378] Containers with shoots and insects were placed randomly on a metal rack equipped with LED light and immediately irradiated with light 450 μmol m^{-2} s^{-1}. Experiment was conducted in Plant Growth Room at temperature 24-26^{0}C and photoperiod of 12 h LED light and 12 h dark. Silkworms were allowed to feed on the treated mulberry leaves for 48 h. Food source was replaced once a day. Completely Randomized Design with four replicates for each treatment and 10 insects for each replicate were used in experiment. Larvae were considered dead if no movement was detected after mechanical stimulation with a paintbrush. The number of live and dead insects were recorded. Insect mortality was assessed for up to

72 h hours after treatment (HAT- hours after treatment). Mulberry leaves were assessed for phytotoxicity symptoms.

[0379] Zn-Ce_6-mix-$DMAE^{15,17}$ amide and Pd-Ce_6-mix-$DMAE^{15,17}$ amide were formulated with propylene glycol and Pluronic F-127 surfactants to improve solubility in water.

Table 12: Effect of photosensitizer on Silkworm larvae Mortality.

	Treatment	Larvae mortality, %		Larva weight reduction, %
#		48 HAT	72 HAT	72HAT
1	Control (water)	0	15	0
2	0.1% Ce_6-mono-3TP-PEG_{400}^{15} amide	0	17.5	32
3	0.1% Cu-Ce_6-mix-$DMAE^{15,17}$ amide	0	12.5	14
4	0.1% Ce_6-mix-$DMAE^{15,17}$ amide	17.5	57.5	89
5	0.1% Zn-Ce_6-mix-$DMAE^{15,17}$ amide + Surfactants	12.5	32.5	44
6	0.1% Pd-Ce_6-mix-$DMAE^{15,17}$ amide + Surfactants	10	35	59
7	Surfactants	2.5	15	19

* Surfactants (0.5% propylene glycol + 0.1% Pluronics F-127)

[0380] Treatments 0.1% Ce_6-mix-$DMAE^{15,17}$ amide and 0.1% Pd-Ce_6-mix-$DMAE^{15,17}$ amide + 0.5%Propylene glycol + 0.1% Pluronic F127 caused larvae mortality 57.5% and 35% respectively and greatly reduced larvae weight.

[0381] Treated mulberry shoots did not display any visible symptoms of phytotoxicity. None of the tested formulations caused phytotoxicity on plant leaves.

Example 17

Control of fungal pathogen *Cgm* on *Nicotiana benthamiana*

[0382] Control of the fungal plant pathogen *Colletotrichum orbiculare* ATC20767 (Cgm) on the host plant *Nicotiana benthamiana* following treatment with modified Chlorin e6 compounds was assessed. Treatments were applied to *N. benthamiana* plants approximately 2 h prior to inoculation with a spore suspension of Cgm. Plants were then exposed to light for a 24-hour period followed by dark incubation until disease symptoms were evident on the

water treated control plants. Once disease symptoms were evident, lesions were counted, and leaf area measured in order to determine the number of lesions/cm^2 leaf area. Four replicate plants were used per treatment and plants were randomized under the light source. Illumination was provided by LED lights emitting about 180 µmol/m^2/s photosynthetically active radiation (PAR). The results are shown in Tables 13 and 14.

Table 13: Effect of modified Ce6 compounds on *Colletotrichum orbiculare*.

Treatment	Disease inhibition, %
0.05% Ce_6-mix-$DMAE^{15,17}$ amide	87
0.05% Zn-Ce_6-mix-$DMAE^{15,17}$ amide	35
0.05% Pd-Ce_6-mix-$DMAE^{15,17}$ amide	1
0.05% Cu-Ce_6-mix-$DMAE^{15,17}$ amide	69
Untreated Control	0

[0383] Surfactants can be added into the solution to increase the solubility of the compounds and spreading on the leaf surfaces.

Table 14: Effect of modified Ce6 compounds on *Colletotrichum orbiculare*.

Treatment	Disease inhibition, %
Untreated Control	0
0.05% Ce_6-mix-$DMAE^{15,17}$ amide + Surfactants	72
0.05% Zn-Ce_6-mix-$DMAE^{15,17}$ amide + Surfactants	97
0.05% Pd-Ce_6-mix-$DMAE^{15,17}$ amide + Surfactants	87
0.05% Cu-Ce_6-mix-$DMAE^{15,17}$ amide + Surfactants	96
0.05% Ce_6-mono-$DMAE^{15}$ amide+ Surfactants	94
Surfactants	-29

* Surfactants (0.5% propylene glycol + 0.1% Pluronics F-127)

[0384] In another experiment, PEG modified Ce6 compounds were tested against Cgm.

Table 15: Effect of modified Ce6 compounds on *Colletotrichum orbiculare*

Treatment	Disease inhibition, %
Control	0
0.05% Ce_6-mono-3TP-PEG_{400}^{15} amide + Surfactants	63
0.05% Zn-Ce_6-mono-3TP-PEG_{400}^{15} amide+ Surfactants	26
Surfactant	12

* Surfactants (0.5% propylene glycol + 0.1% Pluronics F-127)

Example 18

Control of bacterial pathogen *Pst* on *Arabidopsis thaliana*

[0385] *Arabidopsis thaliana* plants were grown under 12 hours:12 hours, light:dark photoperiod, under LED lights (PAR 24 µmol m^{-2} s^{-1}), at a temperature of 25°C ± 3°C and 65% relative humidity. After 3 weeks, plants were sprayed with formulations (50%dilution in water), allowed to dry for 2h, after which *Pseudomonas syringae pv tabacci* (at OD0.08 diluted in 10mM MgCl2) was sprayed. Plants were kept under plastic domes until symptoms develop. Disease severity was rated by counting the number of yellow leaves/plant. Data are average of 3 replicas.

Table 16: Effect of modified Ce6 compounds on bacterial pathogen *Pst* on *Arabidopsis thaliana*

Treatment	Disease inhibition, %
Untreated Control	0
0.05% Ce_6-mix-$DMAE^{15,17}$ amide + surfactants	48
0.05% Zn-Ce_6-mix-$DMAE^{15,17}$ amide + surfactants	45
0.05% Pd-Ce_6-mix-$DMAE^{15,17}$ amide + surfactants	52
0.05% Cu-Ce_6-mix-$DMAE^{15,17}$ amide + surfactants	34
0.05% Ce_6-mono-$DMAE^{15}$ amide + surfactants	56
0.05% Ce_6-mono-3TP-$PEG_{400}{}^{15}$ amide + surfactants	22
0.05% Zn-Ce_6-mono-3TP-$PEG_{400}{}^{15}$ amide + surfactants	34
surfactants	0

* Surfactants (0.5% propylene glycol + 0.1% Pluronics F-127)

Example 19

Control of *Pseudomonas syringae* pv. *tabaci (Pst)* on Nicotiana benthamiana

[0386] Control of the bacterial plant pathogen *Pseudomonas syringae* pv. *tabaci* (Pst) on the host plant *Nicotiana benthamiana* following treatment with modified Chlorin e6 compounds was assessed. Treatments were applied to *N. benthamiana* plants approximately 2 h prior to inoculation with a spore suspension of Cgm. Plants were then exposed to light for a 24-hour period followed by dark incubation until disease symptoms were evident on the water treated control plants. Once disease symptoms were evident, lesions were counted, and leaf area measured in order to determine the number of lesions/cm^2 leaf area. Four replicate plants were used per treatment and plants were randomized under the light source. Illumination was

provided by LED lights emitting about 180 µmol/m^2/s photosynthetically active radiation (PAR). The results are shown in Table 17.

Table 17: Effect of modified Ce6 on *Pseudomonas syringae* pv. *tabaci (Pst)* on Nicotiana benthamiana

	Disease inhibition, %
Untreated Control	0
0.1% Zn-Ce_6-mono-3TP-PEG_{400}^{15} amide	47
0.1% Ce_6-mono-3TP-PEG_{400}^{15} amide	63
0.1% Pd-Ce_6-mix-$DMAE^{15,17}$ amide + surfactants	65
surfactants	34

[0387] * Surfactants (0.5% Propylene glycol + 0.1% Pluronics F-127)

Example 20

Control of Rose aphids with modified Ce6 compounds

[0388] Experiment was conducted to evaluate the toxicity of chlorine derivatives for insect pest Rose aphid (*Marcosiphum rosae*). The experiment was conducted on rosebushes (cv Knockout, Double red) infested with aphids. Experiment was carried out in Plant Nursery (Crop Inspection Service, California, Valley center, USA). Experimental plants were not exposed to pesticide treatments before testing.

[0389] Experimental rose plants were grown outdoor in 3-gal black plastic pots filled with Sunshine #4 soil mix. Plants were irrigated every day and soluble fertilizer 20-20-20 at 200ppm was applied twice weekly.

[0390] Newly infested with aphid nymphs tips of rose plant shoots were used in experiment. Numbers of Rose aphids in colonies congregating on the tips of shoots were counted prior to the treatment and treated shoots were covered with white 4x6" mesh Organza bags (ULINE, USA) to avoid infestation by natural enemies. Bags were kept on shoots during the trial. Upon initiation of the experiment the aphids population (on shoots) was considered uniform with 25-28 aphids per shoot. A completely randomized design was used with 6 replicates plants (one shoot per plant).

[0391] Treatments were applied using 2 oz plastic hand-held spray bottle (Natural Cylinder Spray Bottle, ULINE, Canada) delivering uniform fine spay on plant shoots. Rose shoots were

thoroughly sprayed with tested treatments and exposed to direct sunlight. A second application of treatments was made 7 days after the first application using the same methodology.

[0392] The effect of treatments on insects was determined by live insects count at 7 after 1st treatment and 14 days after 2nd treatment.

[0393] Plants were evaluated for phytotoxicity at 6 days after each foliar spray.

Table 18. Effect of chlorin derivatives on Rose aphids.

	Treatment	Insects suppression, %	
#		7 DAT1	14 DAT2
1	Control (water)	0	0
2	0.1% Ce6-mono-3TP-PEG_{400}^{15} amide	40	65
3	0.1% Cu-Ce6-mix-$DMAE^{15,17}$ amide	76	18
4	0.1% Ce6-mix-$DMAE^{15,17}$ amide	45	66

[0394] Treatments with 0.1% Ce6-mono-3TP-$PEG400^{15}$ amide and 0.1% Ce6-mix-$DMAE^{15,17}$ amide demonstrated good efficacy against Rose aphids and suppressed insect population in comparison with Water Control treatment.

[0395] Treated rosebushes shoots did not display any visible symptoms of phytotoxicity.

Example 21

Control of Cucumber Mosaic Virus on Bell pepper plants

[0396] Dwarf type bell pepper 'Golden baby belle hybrid' seedlings were transplanted into pots filled with pro-mix at 3-4 leaf stage and placed in a growth chamber with temperature at 26/23 ºC (day/night), 70% relative humidity, and light intensity at 270 µmol m^{-2} s^{-1} with 12 hours photoperiod. A formulation comprising 0.1 wt% Ce6-mix-$DMAE^{15,17}$ amide and surfactant was applied as foliar application on day 7, 14, 21, and 28 after transplanting with a hand-held sprayer until the foliage was covered with the solution completely (~2.5 mL/pot). The plants were well-watered by hand irrigation and fertilized at 0.73 g nitrogen m^{-2} from 28-8-18 complete fertilizer every 2 weeks. Cucumber Mosaic Virus (CMV) inoculation took place 2 hours after 3rd application. For the inoculation, leaf blades (~1 g) of CMV virus-infected tobacco plant was ground in about 1 mL PBS buffer (50 mM, pH 7) with mortar and pestle, a

small amount of carborundum was added to the mixture. Q-tip was used to apply to the upper surface of the top 3 newly developed leaf blades of pepper. A randomized block design with 4 replications were used. The pots were re-arranged randomly in the growth chambers twice a week. Severity of CMV disease development in leaves was measured at day 19, 21, 28, 35, and end of trial. The disease severity was calculated as follows: Disease severity = the number of infected leaves/3 inoculated leaves + number of infected younger leaf/number of total younger leaves.

Table 19: Cucumber mosaic virus (CMV) disease severity

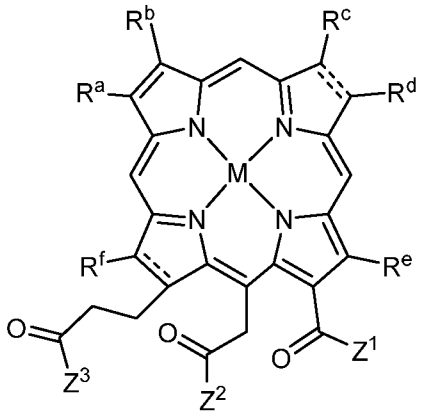
Treatment	**CMV disease severity**					
	Day19	**Day21**	**Day28**	**Day35**	**End of trial**	**Average**
0.1% Ce6-mix-DMAE^{15,17} amide+ Surfactant	0.17	0.42	0.27	0.32	0.55	0.34
Control	0.91	0.92	1.47	1.27	1.48	1.21

*Surfactant:0.1%APG325N

[0397] All publications, patents, and patent documents cited herein above are incorporated by reference herein, as though individually incorporated by reference. The compounds, compositions, methods and uses described herein have been described with reference to various embodiments and techniques. However, one skilled in the art will understand that many variations and modifications can be made while remaining within the spirit and scope of the appended claims.

CLAIMS

1. A compound of Formula I:



Formula I

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

one of Z^2 and Z^3 is NR^2R^3, NR^2-$(CH_2)_n$-NR^4R^5, NR^2-$(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, NR^2-$(CH_2)_n$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-SR^8, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-SR^8, $O(CH_2)_n$-NR^4R^5, $O(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, $O(CH_2)_n$-$O(PO_3H)^-$ W^+, $O(CH_2)_n$-$Si(R^7)_3$, $O(CH_2)_n$-SR^8, $O(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+ or $O(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$; and

the other one of Z^2 and Z^3 is OR^{12};

or

Z^2 is NR^2R^3, NR^2-$(CH_2)_n$-NR^4R^5, NR^2-$(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, NR^2-$(CH_2)_n$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-SR^8, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-SR^8, $O(CH_2)_n$-NR^4R^5, $O(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, $O(CH_2)_n$-$O(PO_3H)^-$ W^+, $O(CH_2)_n$-$Si(R^7)_3$, $O(CH_2)_n$-SR^8, $O(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+ or $O(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$; and

$Z^3 = Z^2$;

each R^1, R^2 and R^{12} is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

R^3 is alkyl substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

each R^4, R^6, R^8, R^9, R^{10} and R^{11} is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl or $-(CH_2)_q-(CH_2CH_2O)_m-R^{13}$;

R^5 is alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl or $-(CH_2)_q-(CH_2CH_2O)_m-R^{13}$;

R^7 is alkyl, O(alkyl) or O(tri-substituted silyl);

R^{13} is H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl, CO(alkyl), CO(substituted alkyl), CO(alkenyl), CO(substituted alkenyl), CO(alkynyl) or CO(substituted alkynyl);

W^+ is an agriculturally acceptable cation;

Y^- is an agriculturally acceptable anion;

n is an integer selected from 1 to 16;

p is an integer selected from 1 to 16;

q is an integer selected from 0 to 16;

m is an integer selected from 1 to 100;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

$\overline{\overline{\quad\quad}}$ is a single bond or a double bond;

$\overline{\overline{\quad\quad}}$ is a single bond or a double bond; and

M is 2H or a metal species,

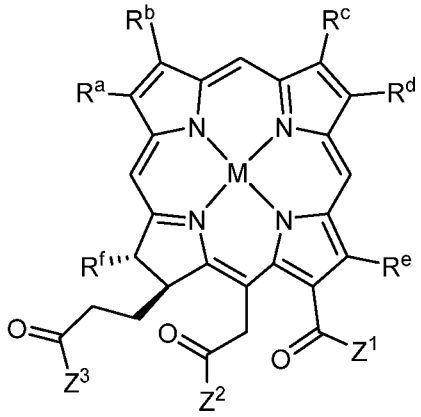
wherein each substituted alkyl, substituted aryl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, CN and N_3.

2. The compound of claim 1, or an agriculturally acceptable salt thereof, wherein:

$\overline{\overline{\quad\quad}}$ is a single bond; and

$\overline{\overline{\quad\quad}}$ is a double bond.

3. The compound of claim 1 or 2, that is represented by Formula I-A1*:



Formula I-A1*

or an agriculturally acceptable salt thereof.

4. The compound of any one of claims 1 to 3, or an agriculturally acceptable salt thereof, wherein:

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, alkyl or alkenyl.

5. The compound of any one of claims 1 to 4, or an agriculturally acceptable salt thereof, wherein:

R^a, R^c, R^e and R^f are methyl;

R^b is vinyl; and

R^d is ethyl.

6. The compound of any one of claims 1 to 5, or an agriculturally acceptable salt thereof, wherein M is 2H.

7. The compound of any one of claims 1 to 5, or an agriculturally acceptable salt thereof, wherein M is a metal species selected from the group consisting of Cu(II), Co(II), Fe(II), Mn(II), Mg(II), Zn(II), Pd(II), Sn(IV), Al(III), Pt(II), Si(IV), Ge(IV), Ga(III) and In(III).

8. The compound of claim 7, or an agriculturally acceptable salt thereof, wherein M is a metal species selected from the group consisting of Cu(II), Pd(II) and Zn(II).

9. The compound of claim 7, or an agriculturally acceptable salt thereof, wherein M is Cu(II).

10. The compound of any one of claims 1 to 9, or an agriculturally acceptable salt thereof, wherein R^1 is H.

11. The compound of any one of claims 1 to 10, or an agriculturally acceptable salt thereof, wherein R^2 is H.

12. The compound of any one of claims 1 to 11, or an agriculturally acceptable salt thereof, wherein R^3 is alkyl.

13. The compound of any one of claims 1 to 12, or an agriculturally acceptable salt thereof, wherein R^4 is H or alkyl.

14. The compound of any one of claims 1 to 13, or an agriculturally acceptable salt thereof, wherein R^5 is alkyl.

15. The compound of any one of claims 1 to 14, or an agriculturally acceptable salt thereof, wherein R^6 is alkyl.

16. The compound of any one of claims 1 to 15, or an agriculturally acceptable salt thereof, wherein R^7 is O(tri-substituted silyl).

17. The compound of any one of claims 1 to 16, or an agriculturally acceptable salt thereof, wherein R^8 is H or alkyl.

18. The compound of any one of claims 1 to 17, or an agriculturally acceptable salt thereof, wherein R^9 is alkyl.

19. The compound of any one of claims 1 to 18, or an agriculturally acceptable salt thereof, wherein R^{10} is alkyl.

20. The compound of any one of claims 1 to 19, or an agriculturally acceptable salt thereof, wherein R^{11} is alkyl.

21. The compound of any one of claims 1 to 20, or an agriculturally acceptable salt thereof, wherein R^{12} is H.

22. The compound of any one of claims 1 to 21, or an agriculturally acceptable salt thereof, wherein R^{13} is H, alkyl, alkenyl, CO(alkyl) or CO(alkenyl).

23. The compound of any one of claims 1 to 22, or an agriculturally acceptable salt thereof, wherein W^+ is selected from the group consisting of sodium, potassium, magnesium and ammonium cations.

24. The compound of any one of claims 1 to 23, or an agriculturally acceptable salt thereof, wherein Y^- is selected from the group consisting of chloride, bromide, phosphate, dimethylphosphate, methylsulfate, ethylsulfate, acetate and lactate.

25. The compound of any one of claims 1 to 24, wherein n is an integer selected from 2 to 4.

26. The compound of any one of claims 1 to 25, wherein p is an integer selected from 2 to 4.

27. The compound of any one of claims 1 to 26, wherein m is an integer selected from 1 to 20.

28. The compound of any one of claims 1 to 27, wherein the substituted alkyl, substituted aryl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br and I.

29. The compound of any one of claims 1 to 28, or an agriculturally acceptable salt thereof, wherein:

Z^2 is NR^2R^3, NR^2-$(CH_2)_n$-NR^4R^5, NR^2-$(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, NR^2-$(CH_2)_n$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-SR^8, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-SR^8, $O(CH_2)_n$-NR^4R^5, $O(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, $O(CH_2)_n$-$O(PO_3H)^-$ W^+, $O(CH_2)_n$-$Si(R^7)_3$, $O(CH_2)_n$-SR^8, $O(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+ or $O(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$; and

Z^3 is OR^{12} or $Z^3 = Z^2$.

30. The compound of any one of claims 1 to 29, or an agriculturally acceptable salt thereof, wherein:

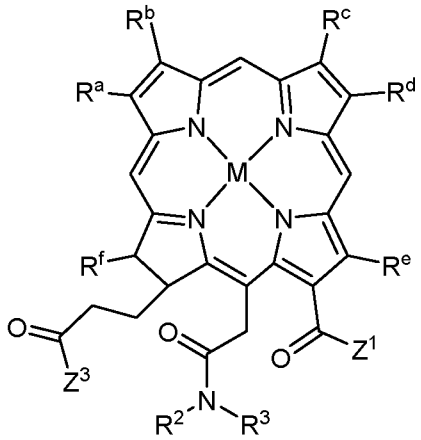
Z^2 is NR^2R^3, NR^2-$(CH_2)_n$-NR^4R^5, NR^2-$(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, NR^2-$(CH_2)_n$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-SR^8 or NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}; and

Z^3 is OR^{12} or $Z^3 = Z^2$.

31. The compound of claim 30, or an agriculturally acceptable salt thereof, wherein Z^3 is OR^{12}.

32. The compound of claim 30, or an agriculturally acceptable salt thereof, wherein $Z^3 = Z^2$.

33. A compound of Formula I-B1:



Formula I-B1

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

R^2 is H, alkyl or substituted alkyl;

R^3 is alkyl or substituted alkyl;

Z^3 is OR^{12} or $Z^3 = NR^2R^3$;

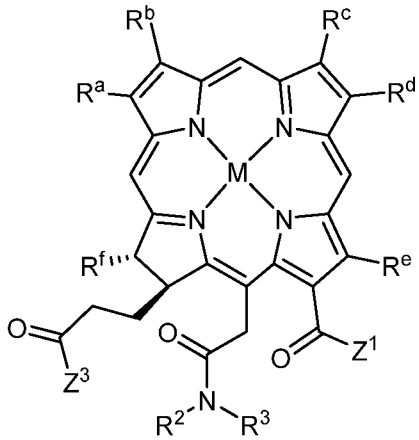
each R^1 and R^{12} is, independently, H, alkyl or substituted alkyl;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, CN and N_3.

34. The compound of claim 33, that is represented by Formula I-B1*:



Formula I-B1*

or an agriculturally acceptable salt thereof.

35. The compound of claim 33 or 34, or an agriculturally acceptable salt thereof, wherein:

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, alkyl or alkenyl.

36. The compound of any one of claims 33 to 35, or an agriculturally acceptable salt thereof, wherein:

R^a, R^c, R^e and R^f are methyl;

R^b is vinyl; and

R^d is ethyl.

37. The compound of any one of claims 33 to 36, or an agriculturally acceptable salt thereof, wherein M is 2H.

38. The compound of any one of claims 33 to 36, or an agriculturally acceptable salt thereof, wherein M is a metal species selected from the group consisting of Cu(II), Co(II), Fe(II), Mn(II), Mg(II), Zn(II), Pd(II), Sn(IV), Al(III), Pt(II), Si(IV), Ge(IV), Ga(III) and In(III).

39. The compound of claim 38, or an agriculturally acceptable salt thereof, wherein M is a metal species selected from the group consisting of Cu(II), Pd(II) and Zn(II).

40. The compound of claim 38, or an agriculturally acceptable salt thereof, wherein M is Cu(II).

41. The compound of any one of claims 33 to 40, or an agriculturally acceptable salt thereof, wherein R^1 is H.

42. The compound of any one of claims 33 to 41, or an agriculturally acceptable salt thereof, wherein R^2 is H.

43. The compound of any one of claims 33 to 42, or an agriculturally acceptable salt thereof, wherein R^3 is alkyl.

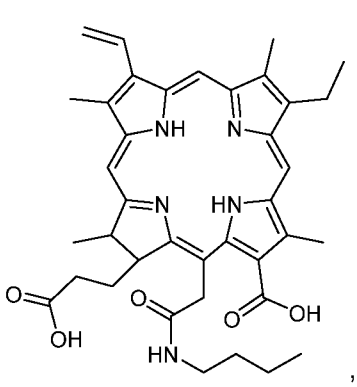
44. The compound of claim 43, or an agriculturally acceptable salt thereof, wherein R^3 is $(C_1\text{-}C_{12})$alkyl.

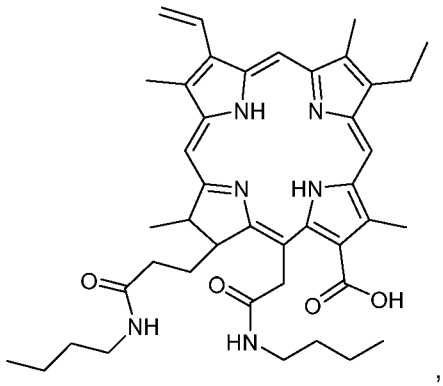
45. The compound of any one of claims 33 to 44, or an agriculturally acceptable salt thereof, wherein R^{12} is H.

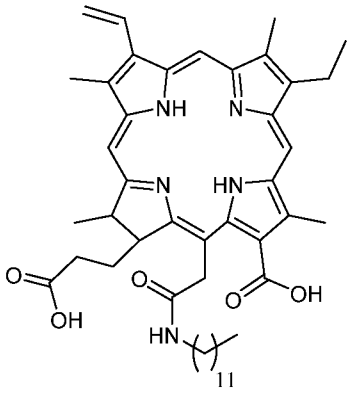
46. The compound of any one of claims 33 to 45, or an agriculturally acceptable salt thereof, wherein Z^3 is OR^{12}.

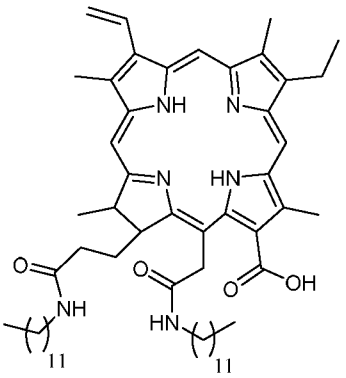
47. The compound of any one of claims 33 to 44, or an agriculturally acceptable salt thereof, wherein $Z^3 = NR^2R^3$.

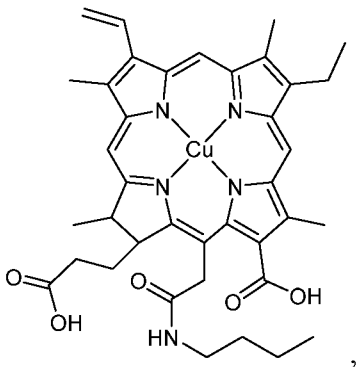
48. The compound of claim 33, that is:

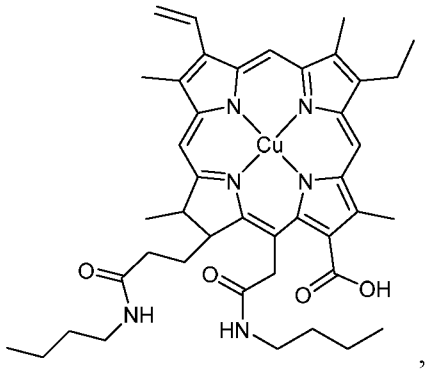


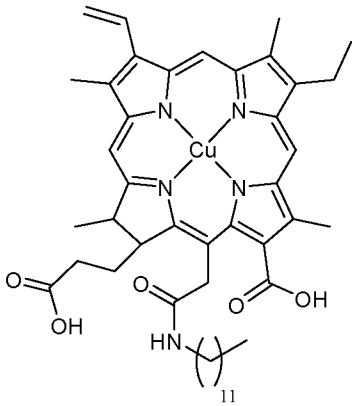
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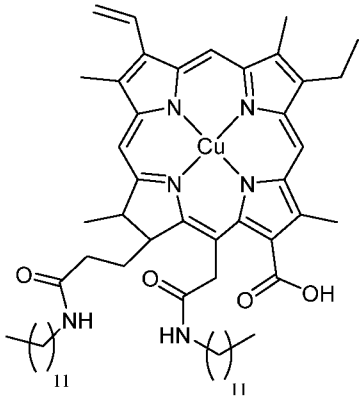
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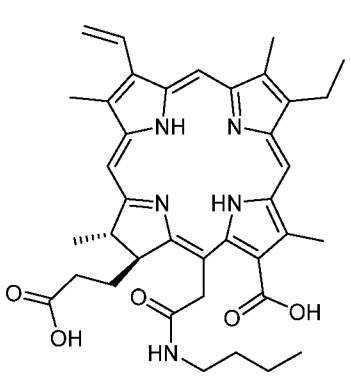
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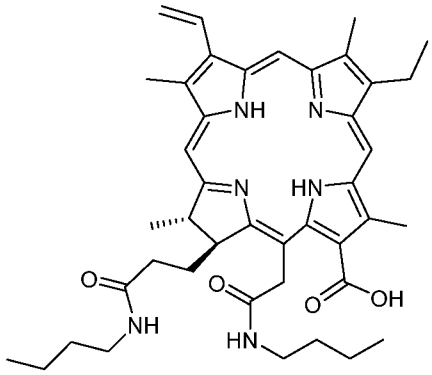
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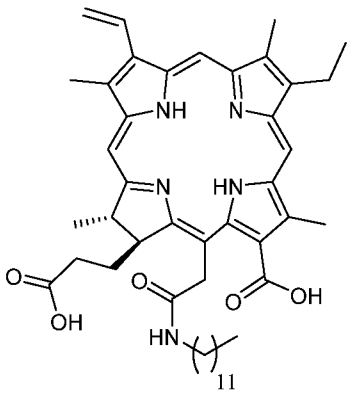
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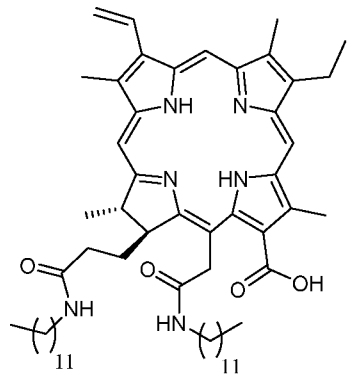
or an agriculturally acceptable salt thereof.

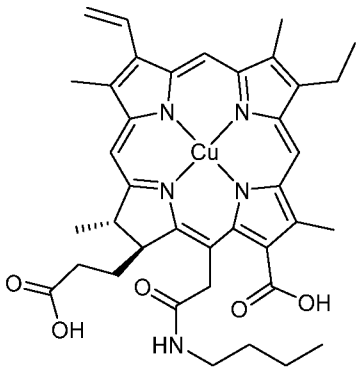
49. The compound of claim 33, that is:

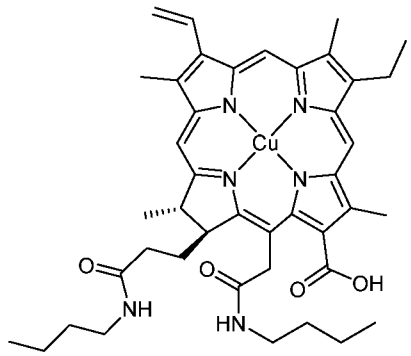


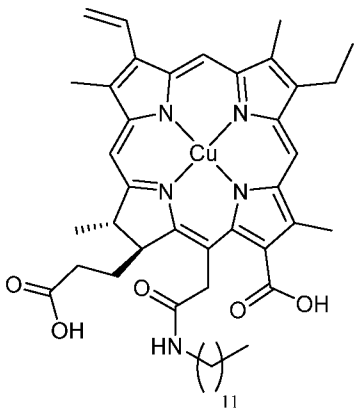
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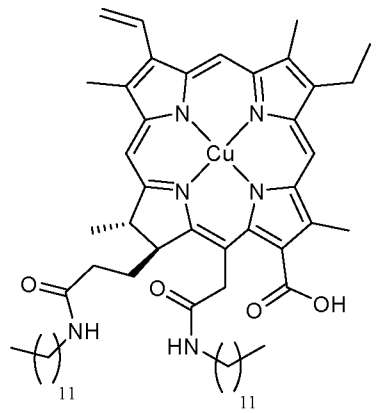
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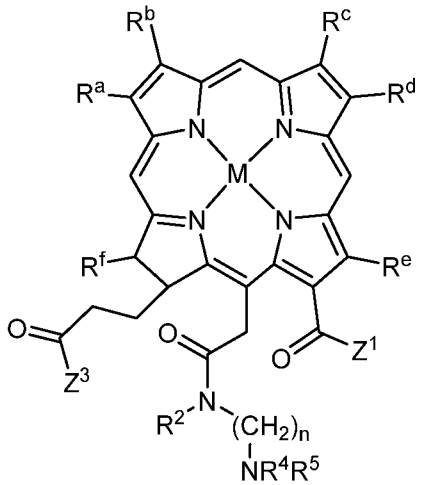
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, or


,

or an agriculturally acceptable salt thereof.

50. A compound of Formula I-B2:



Formula I-B2

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

R^5 is alkyl, substituted alkyl or $-(CH_2)_p-NR^9R^{10}$;

each R^2, R^4, R^9 and R^{10} is, independently, H, alkyl or substituted alkyl;

n is an integer selected from 1 to 16;

p is an integer selected from 1 to 16;

Z^3 is OR^{12} or $Z^3 = NR^2-(CH_2)_n-NR^4R^5$;

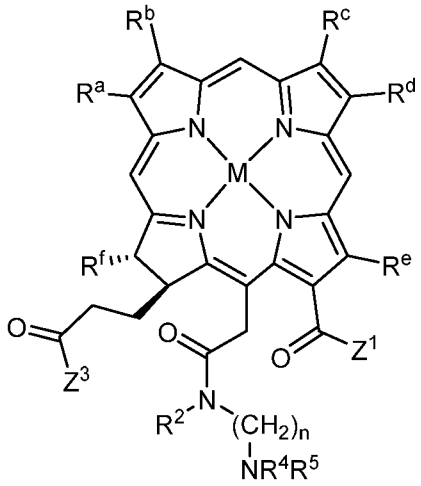
each R^1 and R^{12} is, independently, H, alkyl or substituted alkyl;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, CN and N_3.

51. The compound of claim 50, that is represented by Formula I-B2*:



Formula I-B2*

or an agriculturally acceptable salt thereof.

52. The compound of claim 50 or 51, or an agriculturally acceptable salt thereof, wherein:

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, alkyl or alkenyl.

53. The compound of any one of claims 50 to 52, or an agriculturally acceptable salt thereof, wherein:

R^a, R^c, R^e and R^f are methyl;

R^b is vinyl; and

R^d is ethyl.

54. The compound of any one of claims 50 to 53, or an agriculturally acceptable salt thereof, wherein M is 2H.

55. The compound of any one of claims 50 to 53, or an agriculturally acceptable salt thereof, wherein M is a metal species selected from the group consisting of Cu(II), Co(II), Fe(II), Mn(II), Mg(II), Zn(II), Pd(II), Sn(IV), Al(III), Pt(II), Si(IV), Ge(IV), Ga(III) and In(III).

56. The compound of claim 55, or an agriculturally acceptable salt thereof, wherein M is a metal species selected from the group consisting of Cu(II), Pd(II) and Zn(II).

57. The compound of claim 55, or an agriculturally acceptable salt thereof, wherein M is Cu(II).

58. The compound of any one of claims 50 to 57, or an agriculturally acceptable salt thereof, wherein R^1 is H.

59. The compound of any one of claims 50 to 58, or an agriculturally acceptable salt thereof, wherein R^2 is H.

60. The compound of any one of claims 50 to 59, or an agriculturally acceptable salt thereof, wherein R^4 is H or alkyl.

61. The compound of any one of claims 50 to 60, wherein n is an integer selected from 2 to 4.

62. The compound of any one of claims 50 to 61, or an agriculturally acceptable salt thereof, wherein R^5 is alkyl.

63. The compound of any one of claims 50 to 61, or an agriculturally acceptable salt thereof, wherein R^5 is $-(CH_2)_p-NR^9R^{10}$.

64. The compound of claim 63, or an agriculturally acceptable salt thereof, wherein R^9 is alkyl.

65. The compound of claim 63 or 64, or an agriculturally acceptable salt thereof, wherein R^{10} is alkyl.

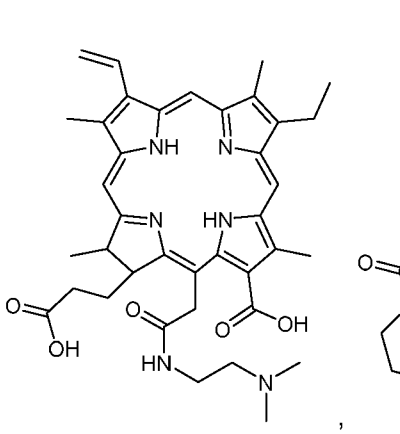
66. The compound of any one of claims 63 to 65, or an agriculturally acceptable salt thereof, wherein p is an integer selected from 2 to 4.

67. The compound of any one of claims 50 to 66, or an agriculturally acceptable salt thereof, wherein R^{12} is H.

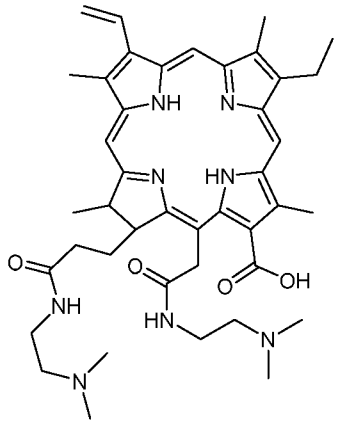
68. The compound of any one of claims 50 to 67, or an agriculturally acceptable salt thereof, wherein Z^3 is OR^{12}.

69. The compound of any one of claims 50 to 67, or an agriculturally acceptable salt thereof, wherein $Z^3 = NR^2\text{-}(CH_2)_n\text{-}NR^4R^5$.

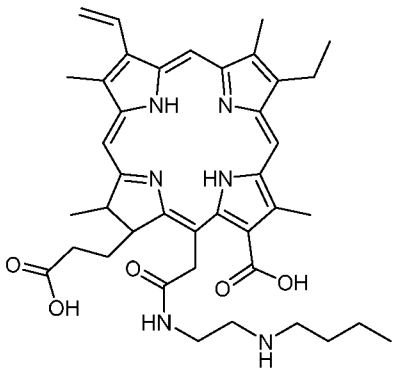
70. The compound of claim 50, that is:



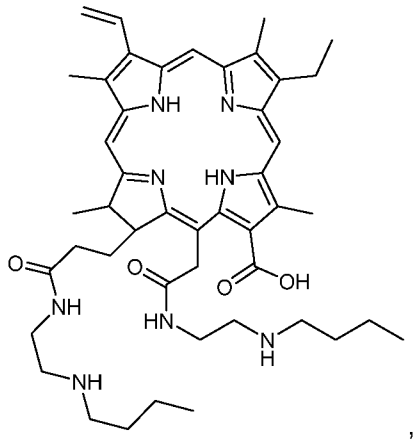
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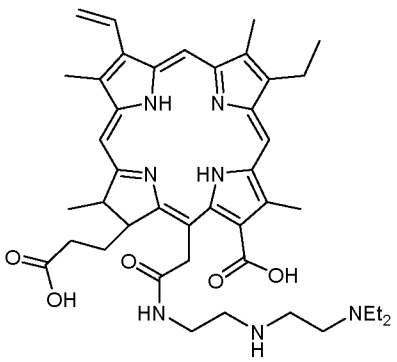
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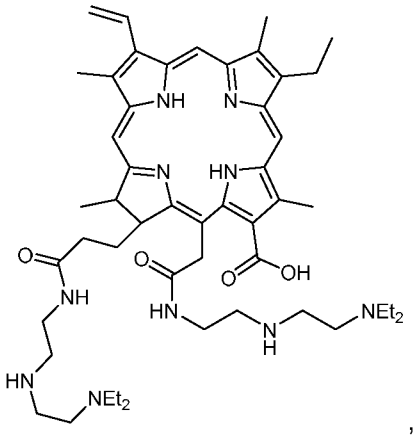
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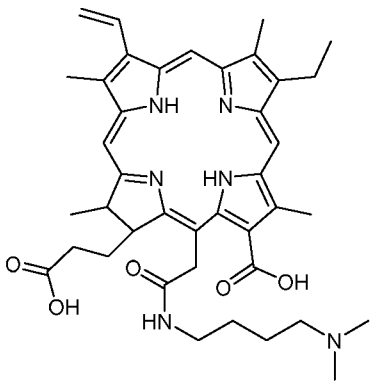
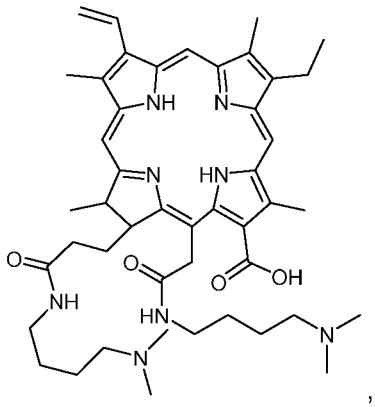
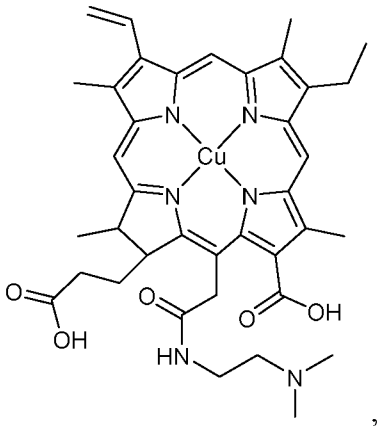
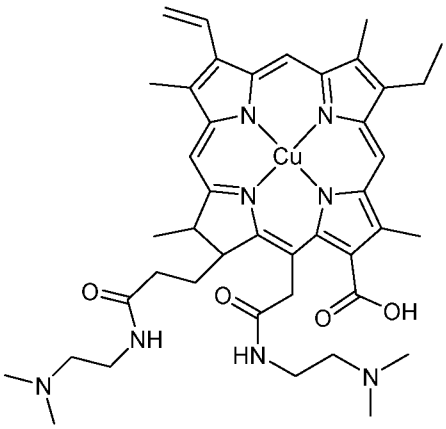
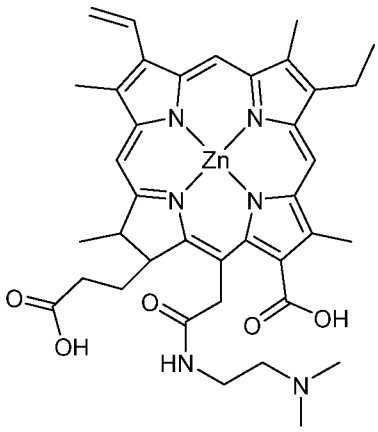
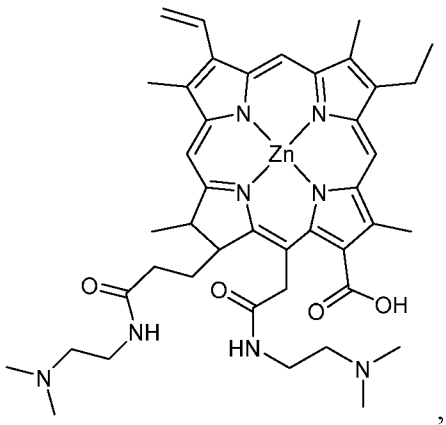
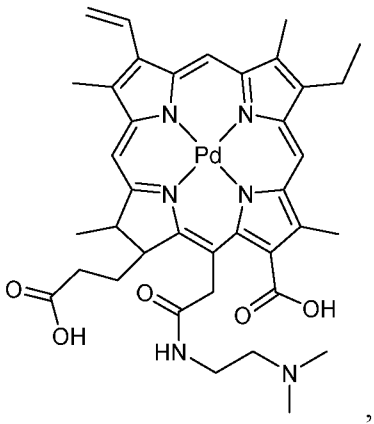
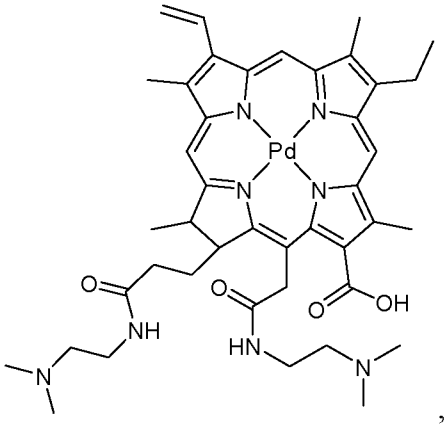
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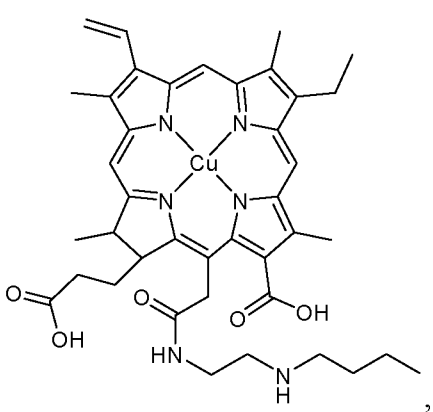
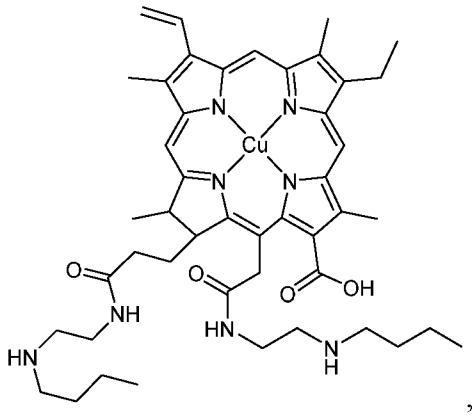
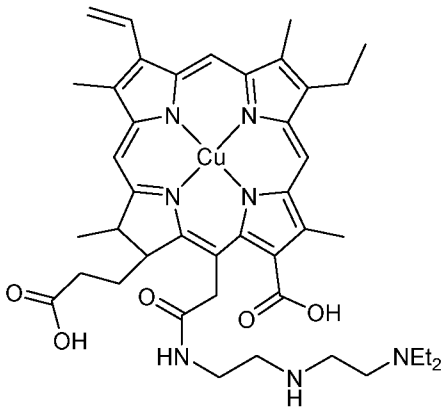
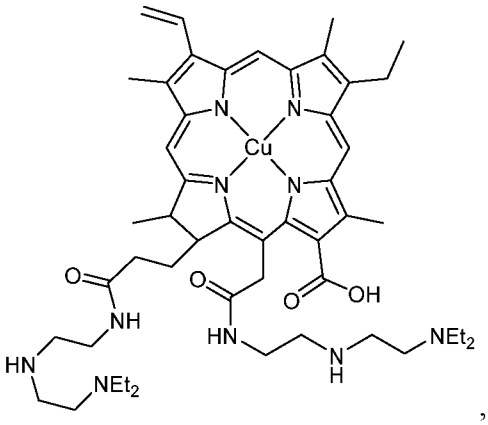
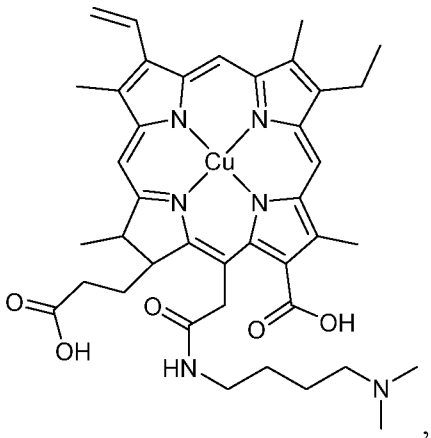
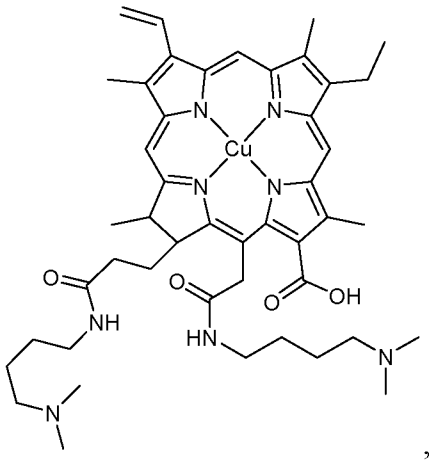


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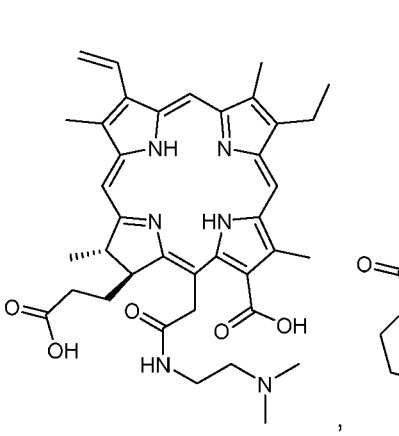
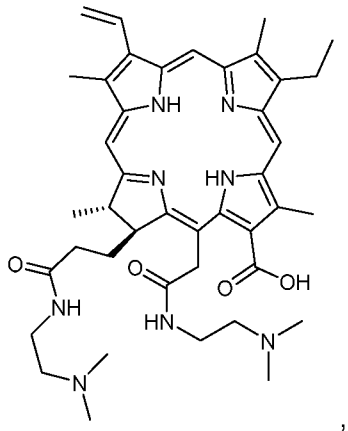
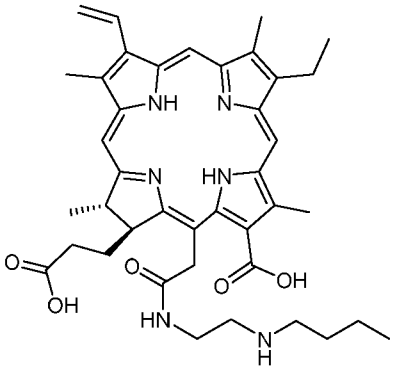
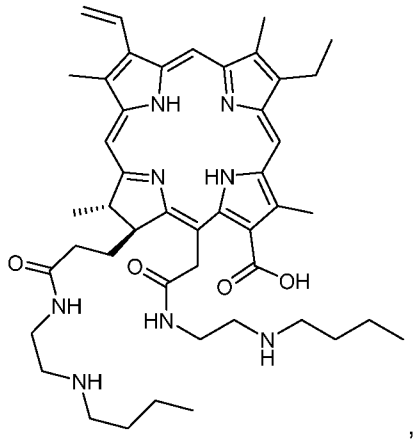
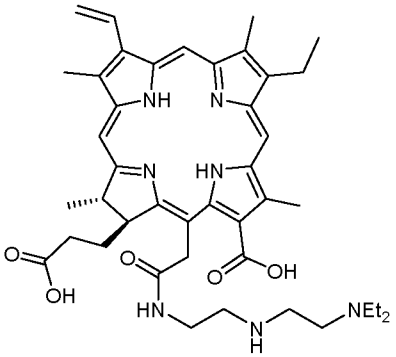
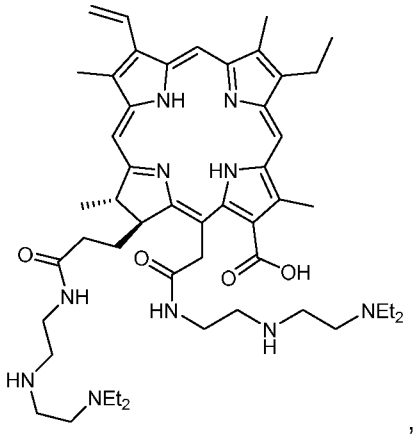
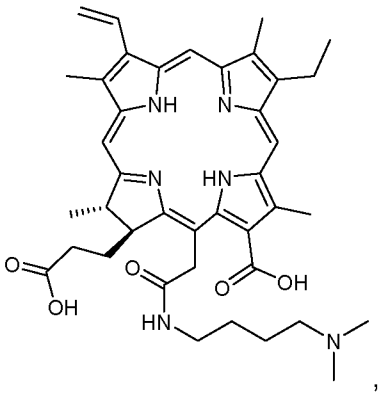
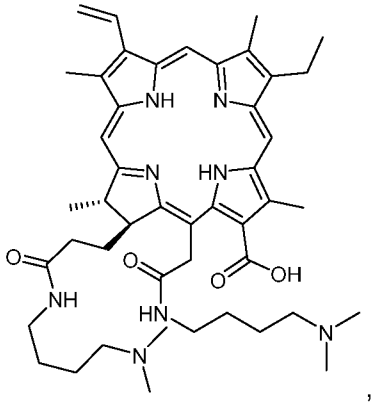
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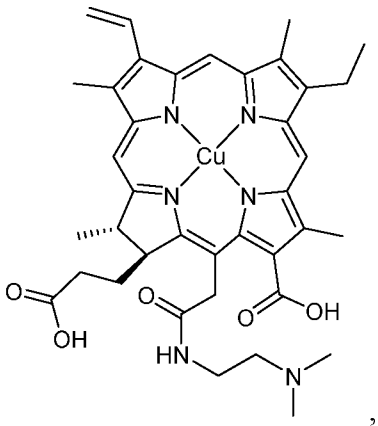
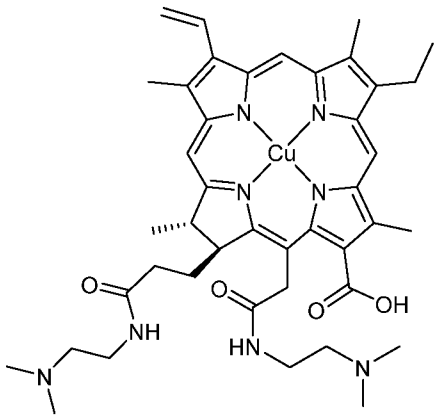
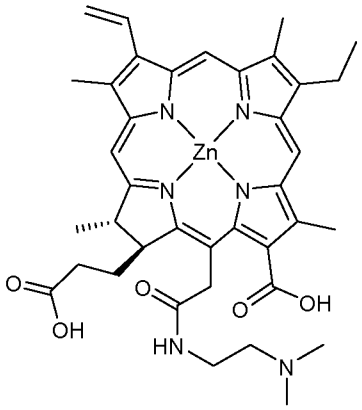
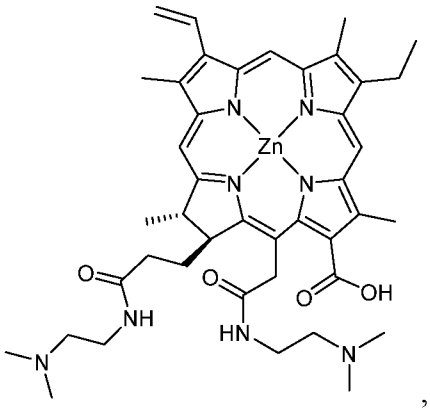
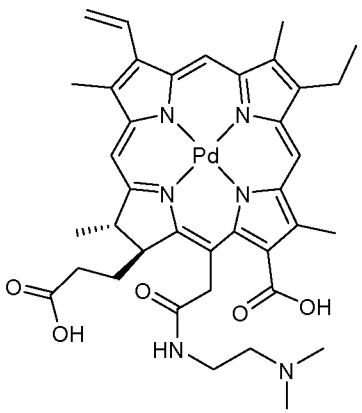
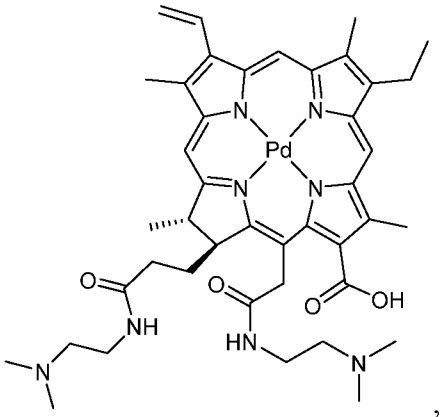
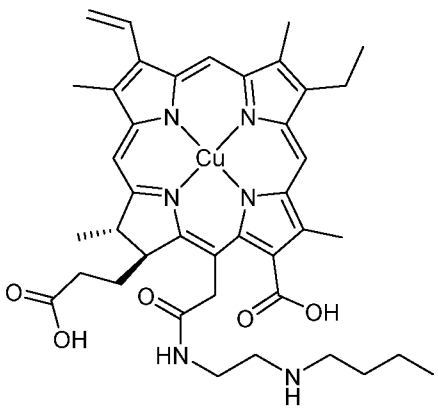
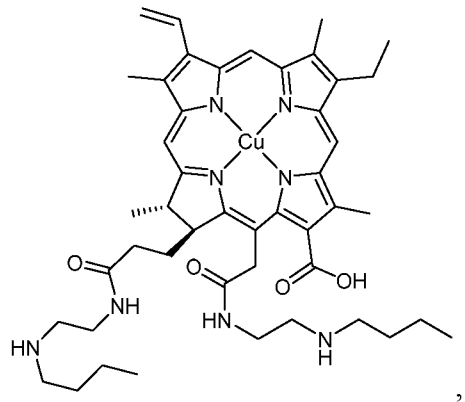

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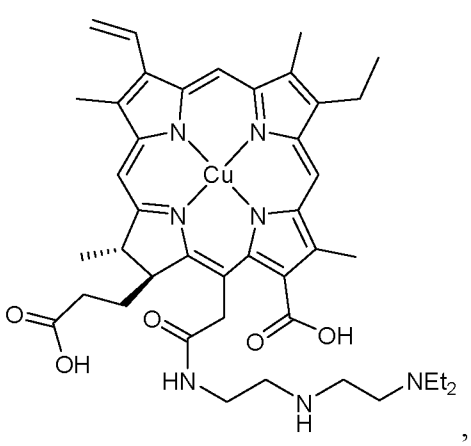

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or an agriculturally acceptable salt thereof.

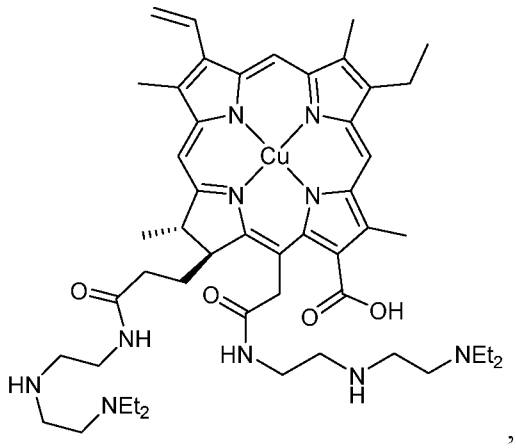
71. The compound of claim 50, that is:


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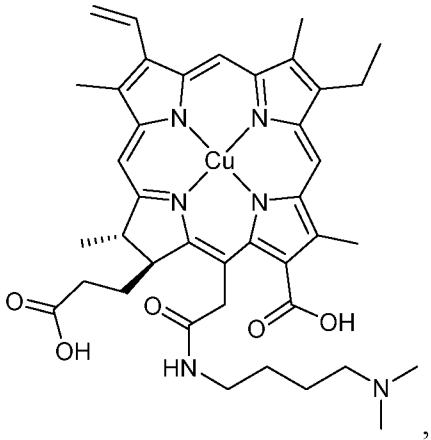

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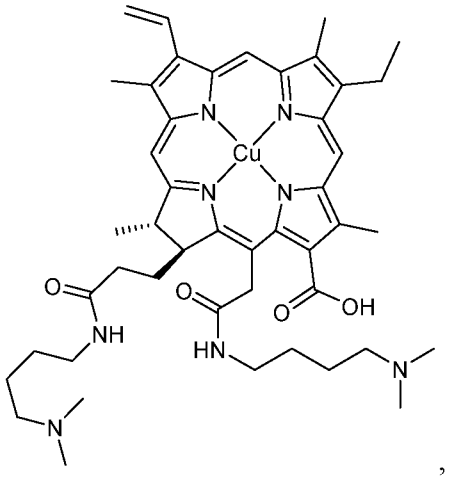
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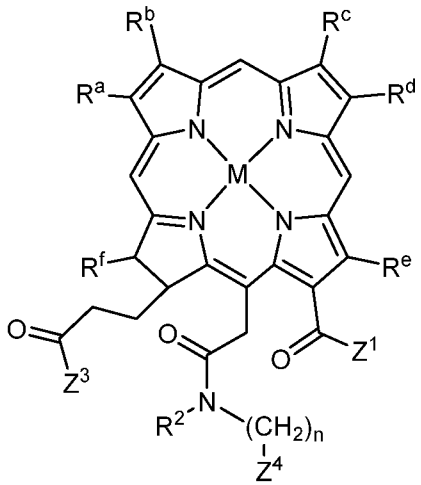
, or



,

or an agriculturally acceptable salt thereof.

72. A compound of Formula I-B3:



Formula I-B3

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

Z^4 is $Si(R^7)_3$ or SR^8;

Z^3 is OR^{12} or $Z^3 = NR^2\text{-}(CH_2)_n\text{-}Z^4$;

each R^1, R^2 and R^{12} is, independently, H, alkyl or substituted alkyl;

R^7 is alkyl, O(alkyl) or O(trisubstituted silyl);

R^8 is H, alkyl, substituted alkyl or $-(CH_2)_q\text{-}(CH_2CH_2O)_m\text{-}R^{13}$;

R^{13} is H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl, CO(alkyl), CO(substituted alkyl), CO(alkenyl), CO(substituted alkenyl), CO(alkynyl) or CO(substituted alkynyl);

n is an integer selected from 1 to 16;

m is an integer selected from 1 to 100;

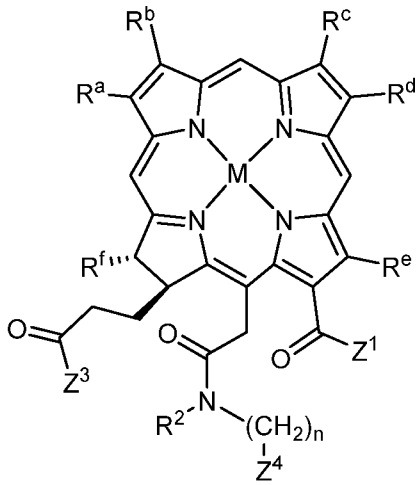
q is an integer selected from 0 to 16;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, CN and N_3.

73. The compound of claim 72, that is represented by Formula I-B3*:



Formula I-B3*

or an agriculturally acceptable salt thereof.

74. The compound of claim 72 or 73, or an agriculturally acceptable salt thereof, wherein:

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, alkyl or alkenyl.

75. The compound of any one of claims 72 to 74, or an agriculturally acceptable salt thereof, wherein:

R^a, R^c, R^e and R^f are methyl;

R^b is vinyl; and

R^d is ethyl.

76. The compound of any one of claims 72 to 75, or an agriculturally acceptable salt thereof, wherein M is 2H.

77. The compound of any one of claims 72to 75, or an agriculturally acceptable salt thereof, wherein M is a metal species selected from the group consisting of Cu(II), Co(II), Fe(II), Mn(II), Mg(II), Zn(II), Pd(II), Sn(IV), Al(III), Pt(II), Si(IV), Ge(IV), Ga(III) and In(III).

78. The compound of claim 77, or an agriculturally acceptable salt thereof, wherein M is a metal species selected from the group consisting of Cu(II), Pd(II) and Zn(II).

79. The compound of claim 77, or an agriculturally acceptable salt thereof, wherein M is Cu(II).

80. The compound of any one of claims 72 to 79, or an agriculturally acceptable salt thereof, wherein R^1 is H.

81. The compound of any one of claims 72 to 80, or an agriculturally acceptable salt thereof, wherein R^2 is H.

82. The compound of any one of claims 72 to 81, or an agriculturally acceptable salt thereof, wherein R^{12} is H.

83. The compound of any one of claims 72 to 82, wherein n is an integer selected from 2 to 4.

84. The compound of any one of claims 72 to 83, or an agriculturally acceptable salt thereof, wherein R^7 is O(tri-substituted silyl).

85. The compound of claims 72 to 83, or an agriculturally acceptable salt thereof, wherein R^8 is $–(CH_2)_q-(CH_2CH_2O)_m-R^{13}$.

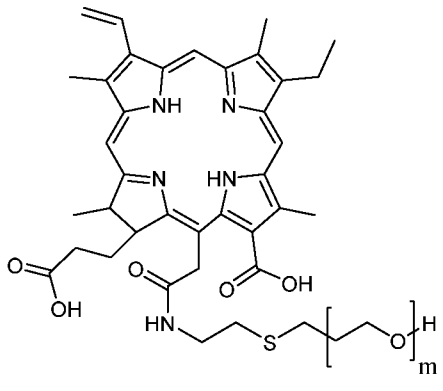
86. The compound of claim 85, or an agriculturally acceptable salt thereof, wherein R^{13} is H.

87. The compound of claim 85 or 86, wherein m is an integer selected from 1 to 20.

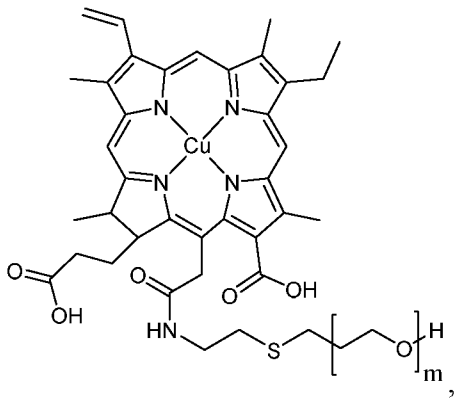
88. The compound of any one of claims 72 to 87, or an agriculturally acceptable salt thereof, wherein Z^3 is OR^{12}.

89. The compound of any one of claims 72 to 87, or an agriculturally acceptable salt thereof, wherein $Z^3 = NR^2-(CH_2)_n-Z^4$.

90. The compound of claim 72, that is:



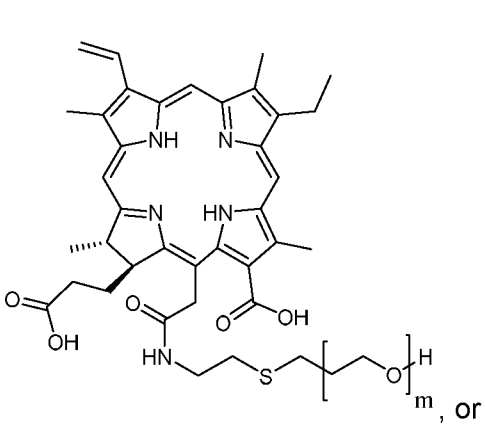
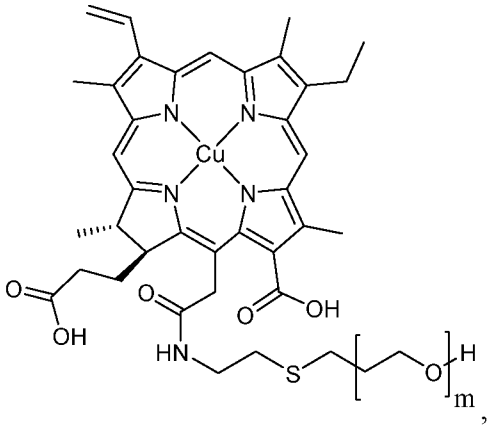
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or an agriculturally acceptable salt thereof,
wherein m is an integer selected from 4 to 15.

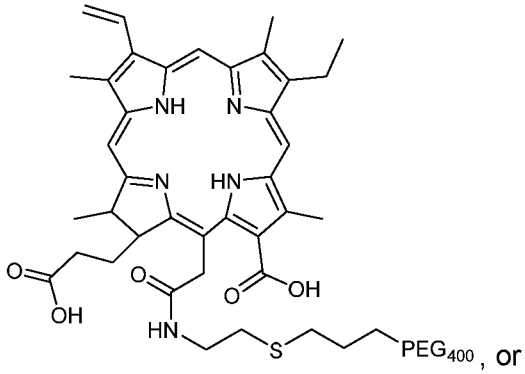
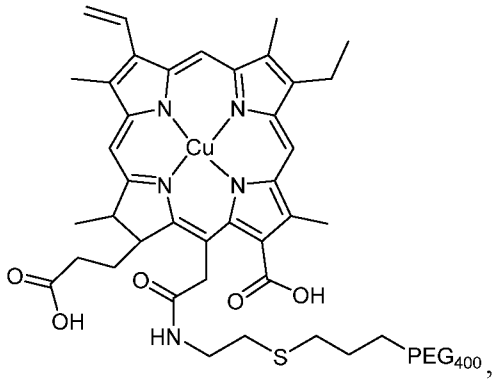
91. The compound of claim 72, that is:

or an agriculturally acceptable salt thereof,

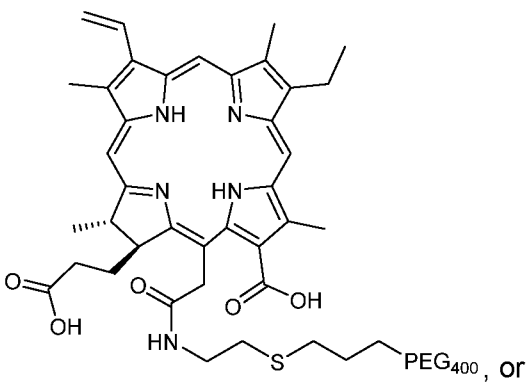
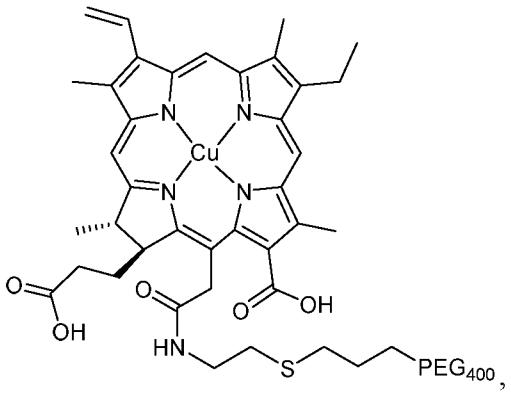
wherein m is an integer selected from 4 to 15.

92. The compound of claim 72, that is:

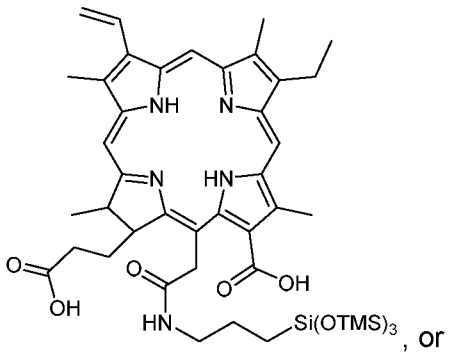
or an agriculturally acceptable salt thereof.

93. The compound of claim 72, that is:

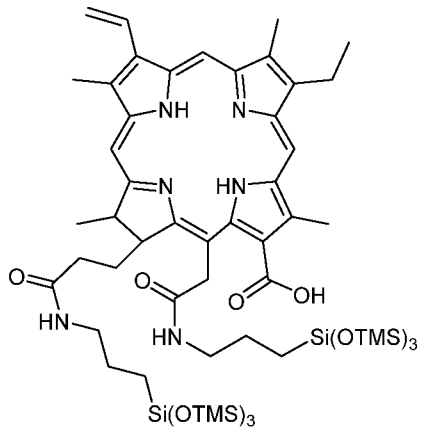



or an agriculturally acceptable salt thereof.

94. The compound of claim 72, that is:

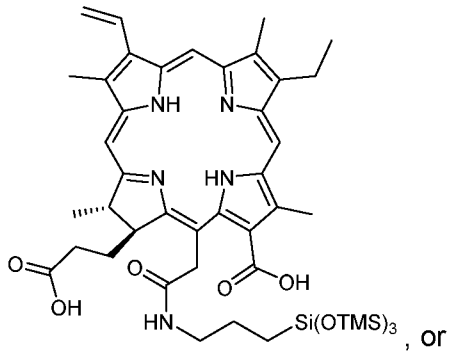


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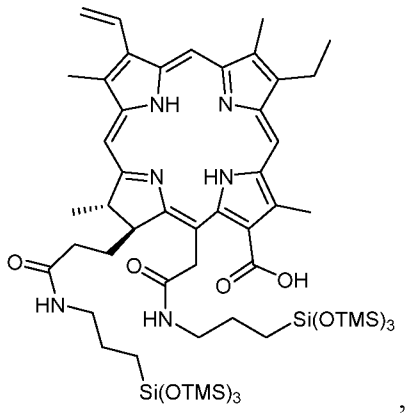


or an agriculturally acceptable salt thereof.

95. The compound of claim 72, that is:



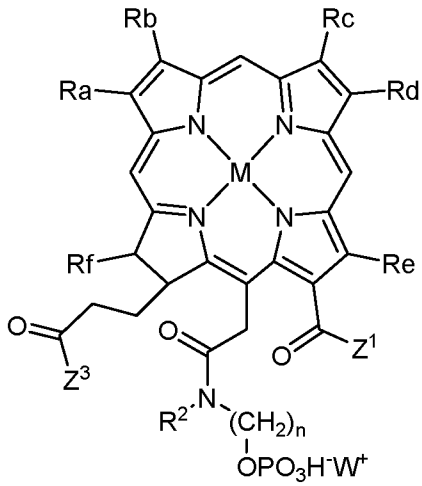
, or



,

or an agriculturally acceptable salt thereof.

96. A compound of Formula I-B4a:



Formula I-B4a

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

Z^3 is OR^{12} or $Z^3 = NR_2\text{-}(CH_2)_n\text{-}O(PO_3H)^- W^+$;

each R^1, R^2 and R^{12} is, independently, H, alkyl or substituted alkyl;

n is an integer selected from 1 to 16;

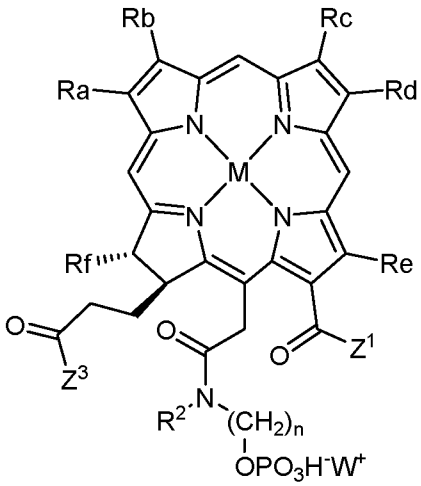
W^+ is an agriculturally acceptable cation;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, CN and N_3.

97. The compound of claim 96, that is represented by Formula I-B4a*:



Formula I-B4a*

or an agriculturally acceptable salt thereof.

98. The compound of claim 96 or 97, or an agriculturally acceptable salt thereof, wherein:

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, alkyl or alkenyl.

99. The compound of any one of claims 96 to 98, or an agriculturally acceptable salt thereof, wherein:

R^a, R^c, R^e and R^f are methyl;

R^b is vinyl; and

R^d is ethyl.

100. The compound of any one of claims 96 to 99, or an agriculturally acceptable salt thereof, wherein M is 2H.

101. The compound of any one of claims 96 to 100, or an agriculturally acceptable salt thereof, wherein M is a metal species selected from the group consisting of Cu(II), Co(II), Fe(II), Mn(II), Mg(II), Zn(II), Pd(II), Sn(IV), Al(III), Pt(II), Si(IV), Ge(IV), Ga(III) and In(III).

102. The compound of claim 101, or an agriculturally acceptable salt thereof, wherein M is a metal species selected from the group consisting of Cu(II), Pd(II) and Zn(II).

103. The compound of claim 101, or an agriculturally acceptable salt thereof, wherein M is Cu(II).

104. The compound of any one of claims 96 to 103, or an agriculturally acceptable salt thereof, wherein R^1 is H.

105. The compound of any one of claims 96 to 104, or an agriculturally acceptable salt thereof, wherein R^2 is H.

106. The compound of any one of claims 96 to 105, or an agriculturally acceptable salt thereof, wherein R^{12} is H.

107. The compound of any one of claims 96 to 106, or an agriculturally acceptable salt thereof, wherein W^+ is selected from the group consisting of sodium, potassium, magnesium and ammonium cations.

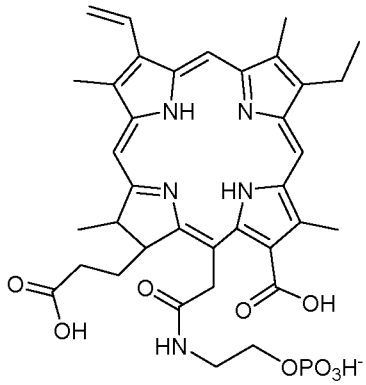
108. The compound of claim 107, wherein W^+ is an ammonium cation.

109. The compound of any one of claims 96 to 108, wherein n is an integer selected from 2 to 4.

110. The compound of any one of claims 96 to 109, or an agriculturally acceptable salt thereof, wherein Z^3 is OR^{12}.

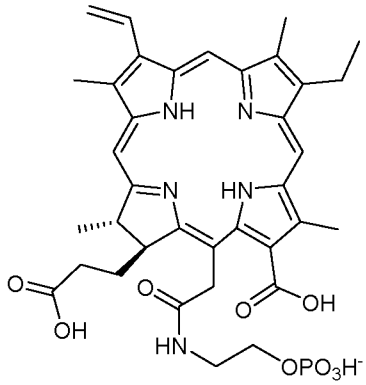
111. The compound of any one of claims 96 to 109, or an agriculturally acceptable salt thereof, wherein $Z^3 = NR_2\text{-}(CH_2)_n\text{-}O(PO_3H)^-W^+$.

112. The compound of claim 96, that is:



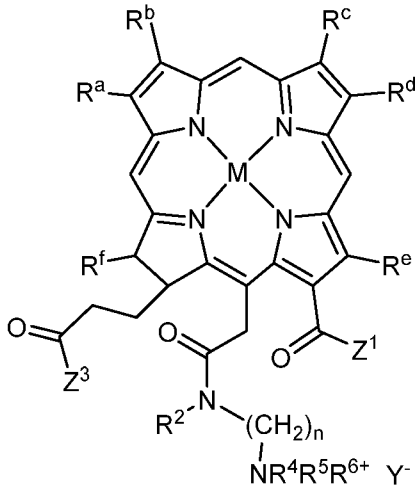
or an agriculturally acceptable salt thereof.

113. The compound of claim 96, that is:



or an agriculturally acceptable salt thereof.

114. A compound of Formula I-B4c:



Formula I-B4c

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

Z^3 is OR^{12} or $Z^3 = NR_2\text{-}(CH_2)_n\text{-}NR^4R^5R^{6+}\ Y^-$;

each R^1, R^2 and R^{12} is, independently, H, alkyl or substituted alkyl;

each R^4, R^5 and R^6 is, independently, alkyl or substituted alkyl;

n is an integer selected from 1 to 16;

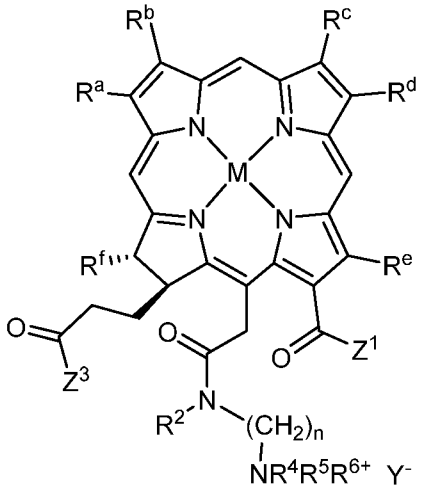
Y^- is an agriculturally acceptable anion;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, CN and N_3.

115. The compound of claim 114, that is represented by Formula I-B4c*:



Formula I-B4c*

or an agriculturally acceptable salt thereof.

116. The compound of claim 114 or 115, or an agriculturally acceptable salt thereof, wherein:

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, alkyl or alkenyl.

117. The compound of any one of claims 114 to 116, or an agriculturally acceptable salt thereof, wherein:

R^a, R^c, R^e and R^f are methyl;

R^b is vinyl; and

R^d is ethyl.

118. The compound of any one of claims 114 to 117, or an agriculturally acceptable salt thereof, wherein M is 2H.

119. The compound of any one of claims 114 to 118, or an agriculturally acceptable salt thereof, wherein M is a metal species selected from the group consisting of Cu(II), Co(II), Fe(II), Mn(II), Mg(II), Zn(II), Pd(II), Sn(IV), Al(III), Pt(II), Si(IV), Ge(IV), Ga(III) and In(III).

120. The compound of claim 119, or an agriculturally acceptable salt thereof, wherein M is a metal species selected from the group consisting of Cu(II), Pd(II) and Zn(II).

121. The compound of claim 119, or an agriculturally acceptable salt thereof, wherein M is Cu(II).

122. The compound of any one of claims 114 to 121, or an agriculturally acceptable salt thereof, wherein R^1 is H.

123. The compound of any one of claims 114 to 122, or an agriculturally acceptable salt thereof, wherein R^2 is H.

124. The compound of any one of claims 114 to 123, or an agriculturally acceptable salt thereof, wherein R^{12} is H.

125. The compound of any one of claims 114 to 124, or an agriculturally acceptable salt thereof, wherein R^4, R^5 and R^6 are alkyl and $R^4 = R^5 = R^6$.

126. The compound of any one of claims 114 to 125, or an agriculturally acceptable salt thereof, wherein Y^- is selected from the group consisting of chloride, bromide, phosphate, dimethylphosphate, methylsulfate, ethylsulfate, acetate, citrate, tartrate and lactate.

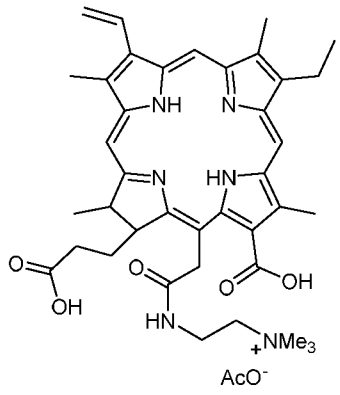
127. The compound of claim 126, wherein Y^- is acetate.

128. The compound of any one of claims 114 to 127, wherein n is an integer selected from 2 to 4.

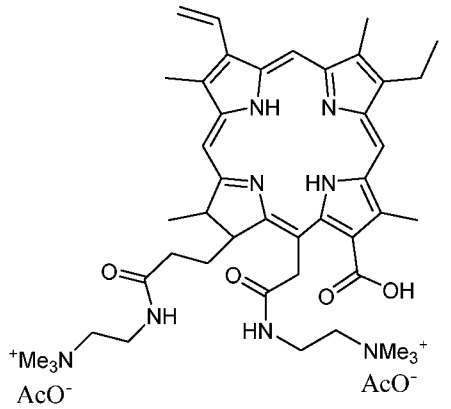
129. The compound of any one of claims 114 to 128, or an agriculturally acceptable salt thereof, wherein Z^3 is OR^{12}.

130. The compound of any one of claims 114 to 129, or an agriculturally acceptable salt thereof, wherein $Z^3 = NR_2\text{-}(CH_2)_n\text{-}NR^4R^5R^{6+}\ Y^-$.

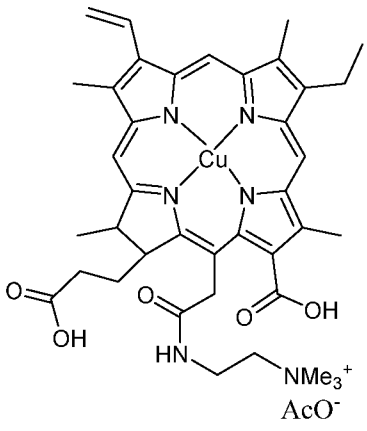
131. The compound of claim 114, that is:

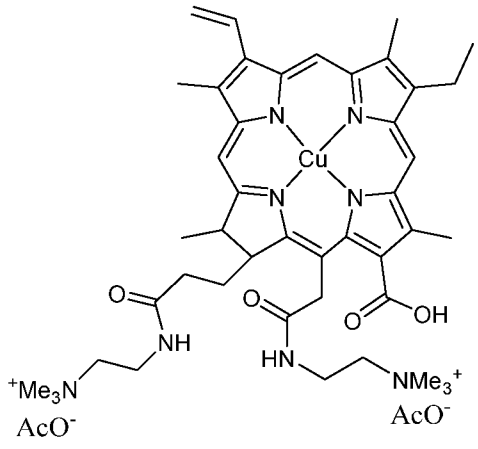


,



,

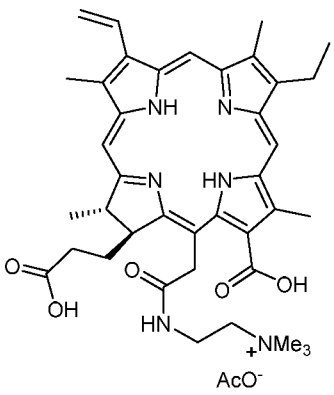




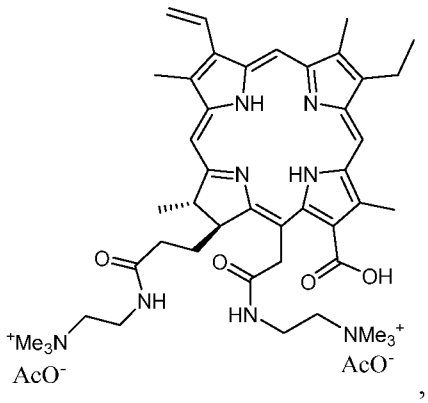
, or

or an agriculturally acceptable salt thereof.

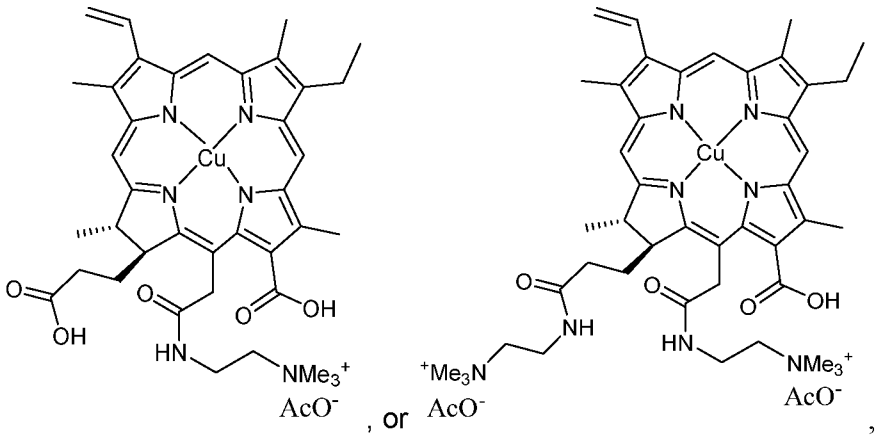
132. The compound of claim 114, that is:



,

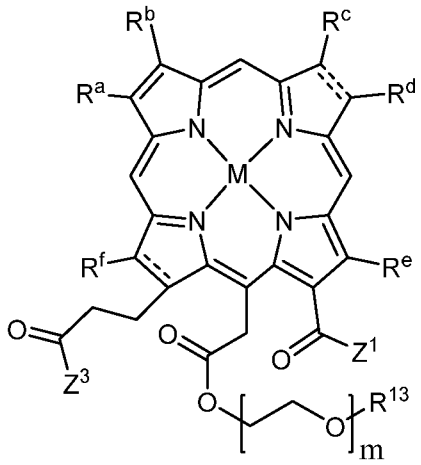


,



or an agriculturally acceptable salt thereof.

133. A compound of Formula I-C:



Formula I-C

or an agriculturally acceptable salt thereof,

wherein:

Z^1 is OR^1;

$Z^3 = OR^{12}$ and m is an integer selected from 1 to 100; or

$Z^3 = O(CH_2CH_2O)_m\text{-}R^{13}$ and m is an integer selected from 5 to 100;

each R^1 and R^{12} is, independently, H, alkyl or substituted alkyl;

R^{13} is H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl, CO(alkyl), CO(substituted alkyl), CO(alkenyl), CO(substituted alkenyl), CO(alkynyl) or CO(substituted alkynyl);

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

------ is a single bond or a double bond;

------ is a single bond or a double bond; and

M is 2H or a metal species,

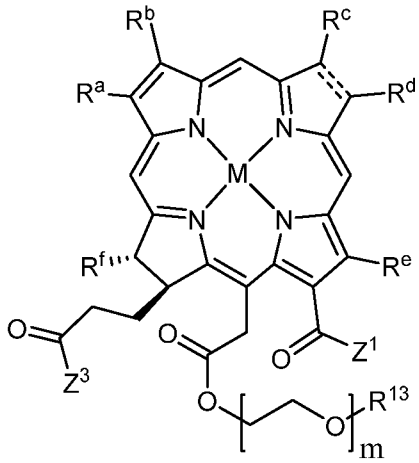
wherein the substituted alkyl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, CN and N_3.

134. The compound of claim 133, or an agriculturally acceptable salt thereof, wherein:

------ is a single bond; and

------ is a double bond.

135. The compound of claim 133 or 134, that is represented by Formula I-C*:



Formula I-C*

or an agriculturally acceptable salt thereof.

136. The compound of any one of claims 133 to 135, or an agriculturally acceptable salt thereof, wherein:

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, alkyl or alkenyl.

137. The compound of any one of claims 133 to 136, or an agriculturally acceptable salt thereof, wherein:

R^a, R^c, R^e and R^f are methyl;

R^b is vinyl; and

R^d is ethyl.

138. The compound of any one of claims 133 to 137, or an agriculturally acceptable salt thereof, wherein M is 2H.

139. The compound of any one of claims 160 to 165, or an agriculturally acceptable salt thereof, wherein M is a metal species selected from the group consisting of Cu(II), Co(II), Fe(II), Mn(II), Mg(II), Zn(II), Pd(II), Sn(IV), Al(III), Pt(II), Si(IV), Ge(IV), Ga(III) and In(III).

140. The compound of claim 139, or an agriculturally acceptable salt thereof, wherein M is a metal species selected from the group consisting of Cu(II), Pd(II) and Zn(II).

141. The compound of claim 139, or an agriculturally acceptable salt thereof, wherein M is Cu(II).

142. The compound of any one of claims 133 to 141, or an agriculturally acceptable salt thereof, wherein R^1 is H.

143. The compound of any one of claims 133 to 142, or an agriculturally acceptable salt thereof, wherein R^{12} is H.

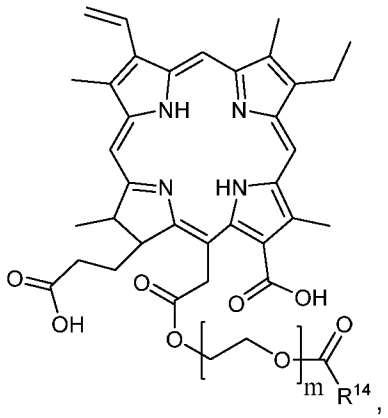
144. The compound of any one of claims 133 to 143, or an agriculturally acceptable salt thereof, wherein R^{13} is alkyl, alkenyl, CO(alkyl) or CO(alkenyl).

145. The compound of any one of claims 133 to 144, wherein m is an integer selected from 5 to 20.

146. The compound of any one of claims 133 to 145, or an agriculturally acceptable salt thereof, wherein Z^3 is OR^{12}.

147. The compound of any one of claims 133 to 145, or an agriculturally acceptable salt thereof, wherein $Z^3 = O(CH_2CH_2O)_m\text{-}R^{13}$.

148. The compound of claim 133, that is:



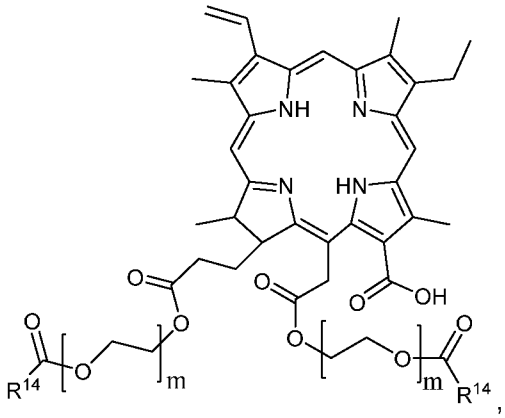
or an agriculturally acceptable salt thereof,

wherein:

m is an integer selected from 1 to 100; and

R^{14} is alkyl or substituted alkyl.

149. The compound of claim 133, that is:



or an agriculturally acceptable salt thereof,

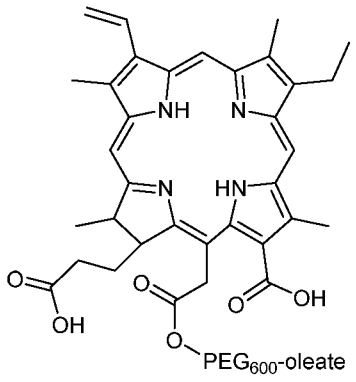
wherein:

m is an integer selected from 5 to 100; and

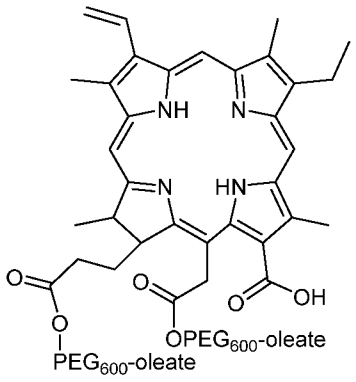
R^{14} is alkyl or substituted alkyl.

150. The compound of claim 148or 149, or an agriculturally acceptable salt thereof, wherein m is an integer selected from 5 to 20.

151. The compound of claim 133, that is:

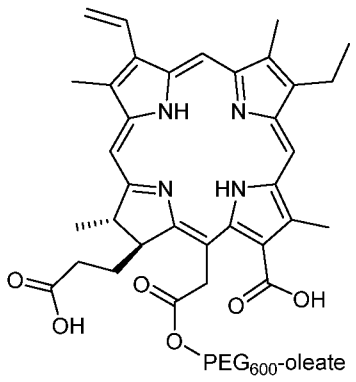


, or

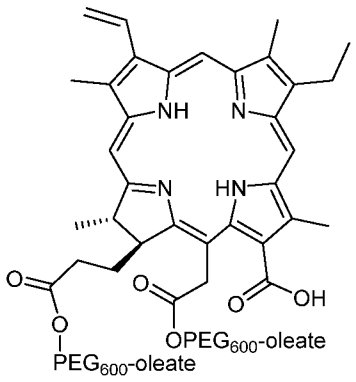


or an agriculturally acceptable salt thereof.

152. The compound of claim 133, that is:

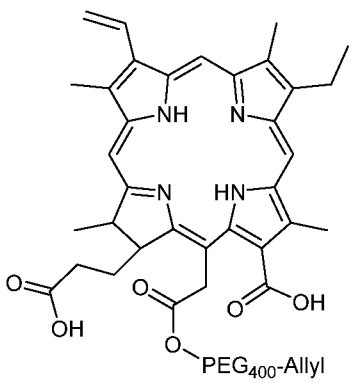


, or

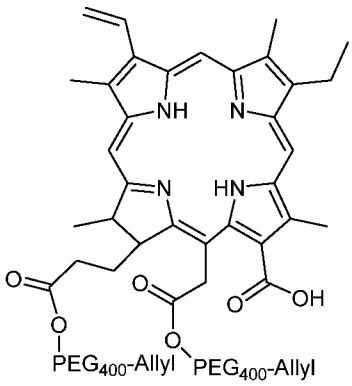


or an agriculturally acceptable salt thereof.

153. The compound of claim 133, that is:



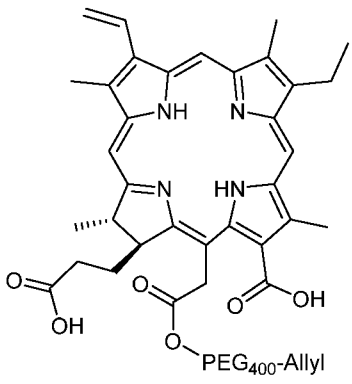
, or



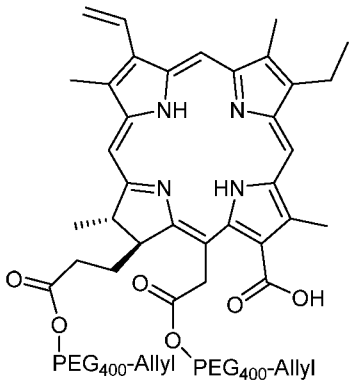
,

or an agriculturally acceptable salt thereof.

154. The compound of claim 133, that is:



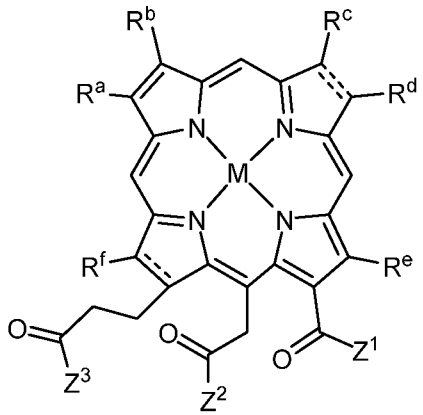
, or



,

or an agriculturally acceptable salt thereof.

155. A compound of Formula I:



Formula I

or an agriculturally acceptable salt thereof, for use in promoting the health of a plant, wherein:

each Z^1, Z^2 and Z^3 is independently OR^1 or NR^2R^3;

each R^1, R^2 and R^3 is independently H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, or substituted alkynyl, wherein if Z^1, Z^2 and Z^3 are each OR^1 then at least one R^1 is not H and if Z^1, Z^2 and Z^3 are each NR^2R^3 then at least one R^3 is not H;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

$\overline{\quad\quad}$ is a single bond or a double bond;

$\overline{\quad\quad}$ is a single bond or a double bond; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted aryl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more -X, $-R^B$, $-O^-$, =O, $-OR^B$, $-SR^B$, $-S^-$, $-NR^B_2$, $Si(R^C)_3$, $-N^+R^B_3$, $-NR^B$-(Alk)-NR^B_2, $-NR^B$-(Alk)-$N^+R^B_3$, $-NR^B$-(Alk)-OR^B, $-NR^B$-(Alk)-$OP(=O)(OR^B)(O^-)$, $-NR^B$-(Alk)-$OP(=O)(OR^B)_2$, $-NR^B$-(Alk)-$Si(R^C)_3$, $-NR^B$-(Alk)-SR^B, -O-(Alk)-NR^B_2, -O-(Alk)-$N^+R^B_3$, -O-(Alk)-OR^B, -O-(Alk)-$OP(=O)(OR^B)(O^-)$, -O-(Alk)-$OP(=O)(OR^B)_2$, -O-(Alk)-$Si(R^C)_3$, -O-(Alk)-SR^B, $=NR^B$, $-CX_3$, -CN, -OCN, -SCN, -N=C=O, -NCS, -NO, $-NO_2$, $=N_2$, $-N_3$, $-NHC(=O)R^B$, $-OC(=O)R^B$, $-NHC(=O)NR^B_2$, $-S(=O)_2$-, $-S(=O)_2OH$, $-S(=O)_2R^B$, $-OS(=O)_2OR^B$, $-S(=O)_2NR^B_2$, $-S(=O)R^B$, $-OP(=O)(OR^B)(O^-)$, $-OP(=O)(OR^B)_2$, $-P(=O)(OR^B)_2$, $-P(=O)(O^-)_2$, $-P(=O)(OH)_2$, $-P(O)(OR^B)(O^-)$, $-C(=O)R^B$, -C(=O)X, $-C(S)R^B$, $-C(O)OR^B$, $-C(O)O^-$, $-C(S)OR^B$, $-C(O)SR^B$, $-C(S)SR^B$, $-C(O)NR^B_2$, $-C(S)NR^B_2$ or $-C(=NR^B)NR^B_2$;

each X is independently a halogen: F, Cl, Br or I;

each R^B is independently H, alkyl, aryl, arylalkyl, a heterocycle, an alkyloxy group such as poly(ethyleneoxy), PEG or poly(methyleneoxy), a capped poly(ethyleneoxy), capped PEG or capped polymethyleneoxy, or a protecting group;

the capped poly(ethyleneoxy), capped PEG and capped poly(methyleneoxy) groups being each independently capped with alkyl, aryl, arylalkyl, alkenyl, alkynyl, CO(alkyl), CO(aryl), CO(arylalkyl), CO(alkenyl) or CO(alkynyl);

each R^C is independently alkyl, aryl, arylalkyl, O(alkyl), O(aryl), O(arylalkyl), or O(tri-substituted silyl);

each tri-substituted silyl is independently substituted with three functional groups selected from alkyl, alkenyl, alkynyl, aryl and arylalkyl; and

each Alk is independently alkylene, alkenylene, or alkynylene.

156. The compound of claim 155, wherein:

Z^1 is OR^1;

one of Z^2 and Z^3 is NR^2R^3 and the other one of Z^2 and Z^3 is OR^1.

157. The compound of claim 155, wherein:

Z^1 is OR^1;

Z^2 is NR^2R^3 and $Z^3 = Z^2$.

158. The compound of any one of claim 155 to 157, wherein R^1 is H.

159. The compound of any one of claims 155 to 158, wherein R^2 is H.

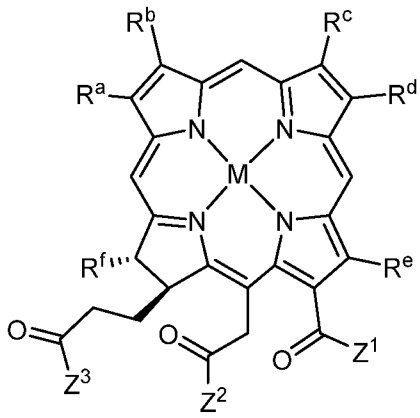
160. The compound of any one of claims 155 to 159, wherein R^3 is alkyl or substituted alkyl.

161. The compound of any one of claims 155 to 160, or an agriculturally acceptable salt thereof, wherein:

$\overline{\quad\quad}$ is a single bond; and

$\overline{\quad\quad}$ is a double bond.

162. The compound of any one of claims 155 to161, that is represented by Formula I-A1*:



Formula I-A1*

or an agriculturally acceptable salt thereof.

163. The compound of any one of claims 155 to 162, or an agriculturally acceptable salt thereof, wherein:

R^a, R^c, R^e and R^f are methyl;

R^b is vinyl; and

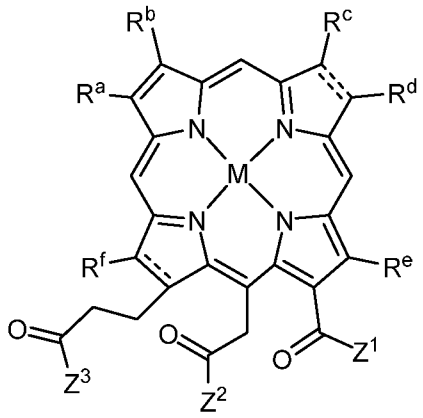
R^d is ethyl.

164. The compound of any one of claims 155 to 163, or an agriculturally acceptable salt thereof, wherein M is 2H or M is a metal species selected from the group consisting of Cu(II), Co(II), Fe(II), Mn(II), Mg(II), Zn(II), Pd(II), Sn(IV), Al(III), Pt(II), Si(IV), Ge(IV), Ga(III) and In(III).

165. The compound of claim 164, or an agriculturally acceptable salt thereof, wherein M is a metal species selected from the group consisting of Cu(II), Pd(II) and Zn(II).

166. The compound of claim 164, or an agriculturally acceptable salt thereof, wherein M is Cu(II).

167. A compound of Formula I:



Formula I

or an agriculturally acceptable salt thereof, for use in promoting the health of a plant, wherein:

Z^1 is OR^1;

one of Z^2 and Z^3 is NR^2R^3, $NR^2\text{-}(CH_2)_n\text{-}NR^4R^5$, $NR^2\text{-}(CH_2)_n\text{-}N^+R^4R^5R^6\ Y^-$, $NR^2\text{-}(CH_2)_n\text{-}O(PO_3H)^-\ W^+$, $NR^2\text{-}(CH_2)_n\text{-}Si(R^7)_3$, $NR^2\text{-}(CH_2)_n\text{-}SR^8$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}NR^9R^{10}$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}N^+R^9R^{10}R^{11}\ Y^-$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}O(PO_3H)^-\ W^+$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}Si(R^7)_3$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}SR^8$, OR^3, $O(CH_2)_n\text{-}NR^4R^5$, $O(CH_2)_n\text{-}N^+R^4R^5R^6\ Y^-$, $O(CH_2)_n\text{-}O(PO_3H)^-\ W^+$, $O(CH_2)_n\text{-}Si(R^7)_3$, $O(CH_2)_n\text{-}SR^8$, $O(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}NR^9R^{10}$, $O(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}N^+R^9R^{10}R^{11}\ Y^-$, $O(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}O(PO_3H)^-\ W^+$ or $O(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}Si(R^7)_3$; and

the other one of Z^2 and Z^3 is OR^{12};

or

Z^2 is NR^2R^3, $NR^2\text{-}(CH_2)_n\text{-}NR^4R^5$, $NR^2\text{-}(CH_2)_n\text{-}N^+R^4R^5R^6\ Y^-$, $NR^2\text{-}(CH_2)_n\text{-}O(PO_3H)^-\ W^+$, $NR^2\text{-}(CH_2)_n\text{-}Si(R^7)_3$, $NR^2\text{-}(CH_2)_n\text{-}SR^8$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}NR^9R^{10}$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}N^+R^9R^{10}R^{11}\ Y^-$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}O(PO_3H)^-\ W^+$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}Si(R^7)_3$, $NR^2\text{-}(CH_2)_n\text{-}NR^4\text{-}(CH_2)_p\text{-}SR^8$, OR^3, $O(CH_2)_n\text{-}NR^4R^5$, $O(CH_2)_n\text{-}N^+R^4R^5R^6\ Y^-$,

$O(CH_2)_n$-$O(PO_3H)^-$ W^+, $O(CH_2)_n$-$Si(R^7)_3$, $O(CH_2)_n$-SR^8, $O(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+ or $O(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$; and

$Z^3 = Z^2$;

each R^1, R^2, R^4, R^6, R^8, R^9, R^{10}, R^{11} and R^{12} is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl or –$(CH_2)_q$-$(CH_2CH_2O)_m$-R^{13};

each R^3 and R^5 is, independently, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl or -$(CH_2)_q$-$(CH_2CH_2O)_m$-R^{13};

R^7 is alkyl, O(alkyl) or O(tri-substituted silyl);

R^{13} is H, alkyl, substituted alkyl, aryl, substituted aryl, CO(alkyl) or CO(substituted alkyl), alkenyl, substituted alkenyl, CO(alkenyl) or CO(substituted alkenyl), alkynyl, substituted alkynyl, CO(alkynyl) or CO(substituted alkynyl);

W^+ is an agriculturally acceptable cation;

Y^- is an agriculturally acceptable anion;

n is an integer selected from 1 to 16;

p is an integer selected from 1 to 16;

q is an integer selected from 0 to 16;

m is an integer selected from 1 to 100;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

------ is a single bond or a double bond;

------ is a single bond or a double bond; and

M is 2H or a metal species,

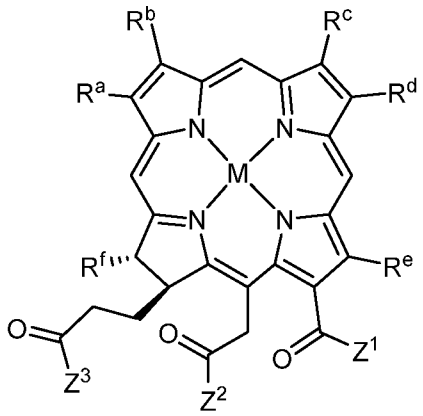
wherein each substituted alkyl, substituted aryl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, CN and N_3.

168. The compound of claim 167, or an agriculturally acceptable salt thereof, wherein:

------ is a single bond; and

------ is a double bond.

169. The compound of claim 166 or 167, that is represented by Formula I-A1*:



Formula I-A1*

or an agriculturally acceptable salt thereof.

170. The compound of any one of claims 166 to 169, or an agriculturally acceptable salt thereof, wherein:

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, alkyl or alkenyl.

171. The compound of any one of claims 166 to 170, or an agriculturally acceptable salt thereof, wherein:

R^a, R^c, R^e and R^f are methyl;

R^b is vinyl; and

R^d is ethyl.

172. The compound of any one of claims 166 to 171, or an agriculturally acceptable salt thereof, wherein M is 2H.

173. The compound of any one of claims 166 to 171, or an agriculturally acceptable salt thereof, wherein M is a metal species selected from the group consisting of Cu(II), Co(II), Fe(II), Mn(II), Mg(II), Zn(II), Pd(II), Sn(IV), Al(III), Pt(II), Si(IV), Ge(IV), Ga(III) and In(III).

174. The compound of claim 173, or an agriculturally acceptable salt thereof, wherein M is a metal species selected from the group consisting of Cu(II), Pd(II) and Zn(II).

175. The compound of claim 173, or an agriculturally acceptable salt thereof, wherein M is Cu(II).

176. The compound of any one of claims 167 to 175, or an agriculturally acceptable salt thereof, wherein R^1 is H.

177. The compound of any one of claims 167 to 176, or an agriculturally acceptable salt thereof, wherein R^2 is H.

178. The compound of any one of claims 167 to 177, or an agriculturally acceptable salt thereof, wherein R^3 is alkyl.

179. The compound of any one of claims 167 to 178, or an agriculturally acceptable salt thereof, wherein R^4 is H or alkyl.

180. The compound of any one of claims 167 to 179, or an agriculturally acceptable salt thereof, wherein R^5 is alkyl.

181. The compound of any one of claims 167 to 180, or an agriculturally acceptable salt thereof, wherein R^6 is alkyl.

182. The compound of any one of claims 167 to 181, or an agriculturally acceptable salt thereof, wherein R^7 is O(tri-substituted silyl).

183. The compound of any one of claims 167 to 182, or an agriculturally acceptable salt thereof, wherein R^8 is $–(CH_2)_q-(CH_2CH_2O)_m-R^{13}$.

184. The compound of any one of claims 167 to183, or an agriculturally acceptable salt thereof, wherein R^9 is alkyl.

185. The compound of any one of claims 167 to 184, or an agriculturally acceptable salt thereof, wherein R^{10} is alkyl.

186. The compound of any one of claims 167 to 185, or an agriculturally acceptable salt thereof, wherein R^{11} is alkyl.

187. The compound of any one of claims 167 to 186, or an agriculturally acceptable salt thereof, wherein R^{12} is H.

188. The compound of any one of claims 167 to 187, or an agriculturally acceptable salt thereof, wherein R^{13} is H, alkyl, alkenyl, CO(alkyl) or CO(alkenyl).

189. The compound of any one of claims 167 to 188, or an agriculturally acceptable salt thereof, wherein W^+ is selected from the group consisting of sodium, calcium, potassium, magnesium, ammonium and alkyl ammonium cations.

190. The compound of any one of claims 167 to 189, or an agriculturally acceptable salt thereof, wherein Y^- is selected from the group consisting of chloride, bromide, phosphate, dimethylphosphate, methylsulfate, ethylsulfate, acetate, citrate, tartrate and lactate.

191. The compound of any one of claims 167 to 190, wherein n is an integer selected from 2 to 4.

192. The compound of any one of claims 167 to 191, wherein p is an integer selected from 2 to 4.

193. The compound of any one of claims 167 to 192, wherein m is an integer selected from 1 to 20.

194. The compound of any one of claims 167 to 193, wherein the substituted alkyl, substituted aryl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, CN and N_3.

195. The compound of any one of claims 167 to 195, or an agriculturally acceptable salt thereof, wherein:

Z^2 is NR^2R^3, NR^2-$(CH_2)_n$-NR^4R^5, NR^2-$(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, NR^2-$(CH_2)_n$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-SR^8, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-SR^8, OR^3, $O(CH_2)_n$-NR^4R^5, $O(CH_2)_n$-$N^+R^4R^5R^6$ Y^-,

$O(CH_2)_n$-$O(PO_3H)^-$ W^+, $O(CH_2)_n$-$Si(R^7)_3$, $O(CH_2)_n$-SR^8, $O(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$N^+R^9R^{10}R^{11}$ Y^-, $O(CH_2)_n$-NR^4-$(CH_2)_p$-$O(PO_3H)^-$ W^+ or $O(CH_2)_n$-NR^4-$(CH_2)_p$-$Si(R^7)_3$; and

Z^3 is OR^{12} or $Z^3 = Z^2$.

196. The compound of any one of claims 167 to 195, or an agriculturally acceptable salt thereof, wherein:

Z^2 is NR^2R^3, NR^2-$(CH_2)_n$-NR^4R^5, NR^2-$(CH_2)_n$-$N^+R^4R^5R^6$ Y^-, NR^2-$(CH_2)_n$-$O(PO_3H)^-$ W^+, NR^2-$(CH_2)_n$-$Si(R^7)_3$, NR^2-$(CH_2)_n$-SR^8, NR^2-$(CH_2)_n$-NR^4-$(CH_2)_p$-NR^9R^{10}; and

Z^3 is OR^{12} or $Z^3 = Z^2$.

197. The compound of claim 196, or an agriculturally acceptable salt thereof, wherein Z^3 is OR^{12}.

198. The compound of claim 196, or an agriculturally acceptable salt thereof, wherein $Z^3 = Z^2$.

199. A composition, comprising:

at least one compound as defined in any one of claims 1 to 198, or an agriculturally acceptable salt thereof; and

a carrier fluid.

200. The composition of claim 199, further comprising a chelating agent.

201. The composition of claim 200, wherein the chelating agent comprises at least one carboxylic acid group or an agriculturally acceptable salt thereof.

202. The composition of claim 200 or 201, wherein the chelating agent comprises at least two carboxylic acid groups or agriculturally acceptable salts thereof.

203. The composition of any one of claims 200 to 202, wherein the chelating agent comprises at least one amino group or an agriculturally acceptable salt thereof.

204. The composition of any one of claims 200 to 203, wherein the chelating agent comprises an amino-carboxylic acid compound or an agriculturally acceptable salt thereof.

205. The composition of claim 204, wherein the amino-carboxylic acid compound comprises an amino polycarboxylic acid compound or an agriculturally acceptable salt thereof.

206. The composition of any one of claims 200 to 205, wherein the chelating agent is selected from the group consisting of ethylenediaminetetraacetic acid (EDTA) or an agriculturally acceptable salt thereof, ethylenediamine-N,N'-disuccinic acid (EDDS) or an agriculturally acceptable salt thereof, iminodisuccinic acid (IDS) or an agriculturally acceptable salt thereof, and mixtures thereof.

207. The composition of any one of claims 200 to 186, wherein the chelating agent comprises a polyaspartic acid or an agriculturally acceptable salt thereof.

208. The composition of any one of claims 200 to 188, wherein the chelating agent is metallated.

209. The composition of any one of claims 200 to 188, wherein the chelating agent is metal-free.

210. The composition of any one of claims 199 to 209, further comprising a surfactant.

211. The composition of claim 210, wherein the surfactant is selected from the group consisting of an ethoxylated alcohol, a polymeric surfactant, a fatty acid ester, a poly(ethylene glycol), an ethoxylated alkyl alcohol, a monoglyceride, an alkyl monoglyceride and a mixture thereof.

212. The composition of claim 210 or 211, wherein the surfactant comprises a poly(ethylene glycol) of Formula R^{15}-O-$(CH_2CH_2O)_f$-R^{16},

wherein:

each R^{15} and R^{16} is each, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, CO(alkyl) or CO(substituted alkyl); and

f is an integer selected from 1 to 100;

wherein the substituted alkyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, alkenyl, CN and N_3.

213. The composition of claim 212, wherein the substituted alkyl groups are methyl, vinyl or CO(methyl).

214. The composition of any one of claims 199 to 213, further comprising an oil selected from the group consisting of a mineral oil, an essential oil, a vegetable oil and a mixture thereof.

215. The composition of claim 214, wherein the oil comprises a vegetable oil selected from the group consisting of coconut oil, canola oil, soybean oil, rapeseed oil, sunflower oil, safflower oil, peanut oil, cottonseed oil, palm oil, rice bran oil and mixtures thereof.

216. The composition of claim 214 or 215, wherein the oil comprises a mineral oil selected from the group consisting of a paraffinic oil, a branched paraffinic oil, naphthenic oil, an aromatic oil and mixtures thereof.

217. The composition of any one of claims 214 to 216, wherein the oil comprises a poly-alpha-olefin (PAO).

218. The composition of any one of claims 199 to 217, wherein the carrier fluid comprises water.

219. The composition of any one of claims 199 to 218, wherein the carrier fluid comprises an oil-in-water emulsion.

220. A method for promoting the health of a plant, comprising:

applying to the plant the compound as defined in any one of claims 1 to 198 or an agriculturally acceptable salt thereof, or the composition as defined in any one of claims 199 to 219; and

exposing the plant to light.

221. The method of claim 220, wherein promoting the health of the plant comprises preventing or inhibiting growth of a microbial pathogen of the plant.

222. The method of claim 220, wherein promoting the health of the plant comprises inhibiting growth of a microbial pathogen of the plant.

223. The method of claim 221 or 222, wherein the microbial pathogen comprises a fungal pathogen.

224. The method of claim 223, wherein the fungal pathogen comprises at least one of *Botrytis cinerea*, *Alternaria solani* and *Sclerotinia homoeocarpa*.

225. The method of claim 221 or 222, wherein the microbial pathogen comprises a bacterial pathogen.

226. The method of claim 225, wherein the bacterial pathogen comprises Gram negative bacteria.

227. The method of claim 226, wherein the bacterial pathogen comprises at least one of *Erwinia amylovora, Xanthomonas axonopodis*, and *E. Coli.*

228. The method of claim 221 or 222, wherein the microbial pathogen comprises a virus, a viroid, a virus-like organism or a phytoplasma.

229. The method of claim 228, wherein the microbial pathogen comprises a virus.

230 The method of claim 229, wherein the virus is Cucumber mosaic virus (CMV).

231. The method of claim 220, wherein promoting the health of the plant comprises increasing resistance of the plant to one or more abiotic stress.

232. The method of claim 231, wherein the one or more abiotic stress is selected from the group consisting of cold stress, heat stress, water stress, transplant shock stress, low light stress, photooxidative stress, drought stress and salinity stress.

233. The method of claim 231 or 232, wherein applying the compound to the plant is performed at or before onset of the one or more abiotic stress.

234. The method of claim 231 or 233, wherein applying the compound to the plant is performed after onset of the abiotic stress.

235. The method of claim 220, wherein promoting the health of the plant comprises controlling a pest of the plant.

236. The method of claim 235, wherein the pest of the plant is selected from the group consisting of insects and insect larvae.

237. The method of claim 235 or 236, wherein applying the compound to the plant is performed at or before contamination of the plant by the pest.

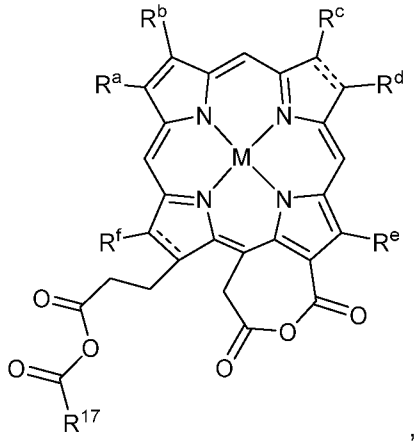
238. The method of claim 235 or 236, wherein applying the compound to the plant is performed after contamination of the plant by the pest.

239. The method of any one of claims 220 to 238, wherein the plant is a non-woody crop plant, a woody plant or a turfgrass.

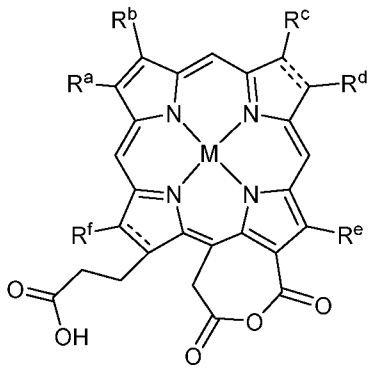
240. The method of claim 239, wherein the plant is a woody plant.

241. The method of claim 240, wherein the woody plant is a tree.

242. A method of manufacturing a compound of Formula II-A and/or Formula II-B:



Formula II-A



Formula II-B

or salts thereof,

wherein:

R^{17} is H, alkyl, aryl or alkoxy;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

⎓ is a single bond or a double bond;

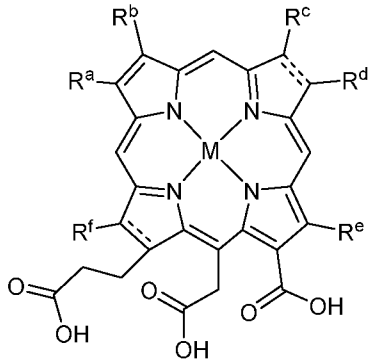
⎓ is a single bond or a double bond; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted aryl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, alkenyl, CN and N_3;

the method comprising:

reacting a compound of Formula III:



Formula III

or a salt thereof, with an anhydride of general formula $(R^{17}CO)_2O$.

243. The method of claim 242, wherein reacting the compound of Formula III with the anhydride of general formula $(R^{17}CO)_2O$ is performed at a temperature of up to 40°C.

244. The method of claim 242 or 243, wherein R^{17} is H, alkyl or aryl, and the compound of Formula II-A is obtained.

245. The method of claim 244, wherein R^{17} is methyl, and substantially all of the product is the compound of Formula II-A.

246. The method of claim 245, wherein the reaction is performed in Ac_2O.

247. The method of claim 242 or 243, wherein R^{17} is alkoxy, and the compound of Formula II-B is obtained.

248. The method of claim 247, wherein R^{17} is tert-butoxy, and substantially all of the product is the compound of Formula II-B.

249. The method of claim 248, wherein the reaction is performed in DCM.

250. The method of any one of claims 242 to 249, wherein:
------ is a single bond; and
------ is a double bond.

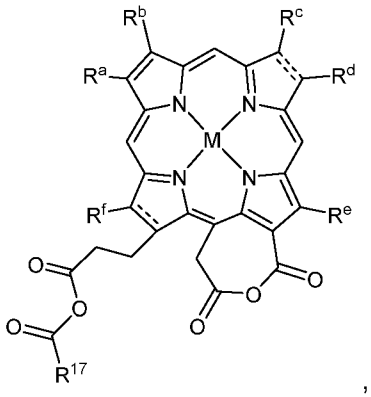
251. The method of any one of claims 242 to 250, wherein:
each R^a, R^b, R^c, R^d, R^e and R^f is, independently, alkyl or alkenyl.

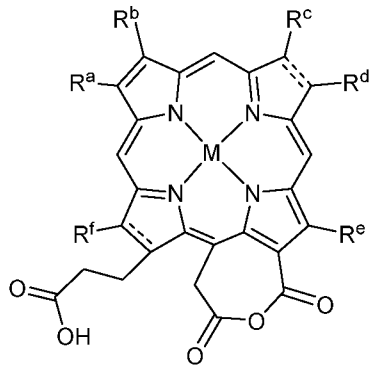
252. The method of any one of claims 242 to 251, wherein:
R^a, R^c, R^e and R^f are methyl;
R^b is vinyl; and
R^d is ethyl.

253. The method of any one of claims 242 to 252, wherein M is 2H.

254. The method of any one of claims 242 to 252, wherein M is a metal species selected from the group consisting of Cu(II), Co(II), Fe(II), Mn(II), Mg(II), Zn(II), Pd(II), Sn(IV), Al(III), Pt(II), Si(IV), Ge(IV), Ga(III) and In(III).

255. A compound of Formula II-A or Formula II-B:





Formula II-A Formula II-B

or a salt thereof,

wherein:

R^{17} is H or alkyl;

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, H, alkyl, substituted alkyl, aryl, substituted aryl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl;

⎓ is a single bond or a double bond;

⎓ is a single bond or a double bond; and

M is 2H or a metal species,

wherein the substituted alkyl, substituted aryl, substituted alkenyl and substituted alkynyl groups are, independently, substituted with one or more F, Cl, Br, I, hydroxy, alkenyl, CN and N_3.

256. The compound of claim 255, or a salt thereof, wherein:

⎓ is a single bond; and

⎓ is a double bond.

257. The compound of any one of claims 255 or 256, or a salt thereof, wherein:

each R^a, R^b, R^c, R^d, R^e and R^f is, independently, alkyl or alkenyl.

258. The compound of any one of claims 255 to 257, or a salt thereof, wherein:

R^a, R^c, R^e and R^f are methyl;

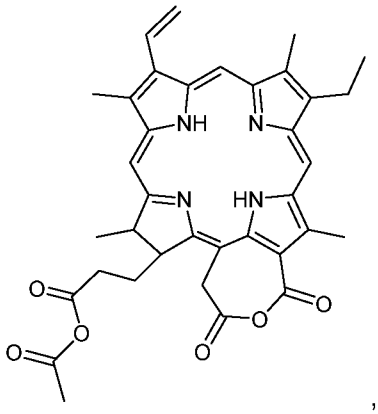
R^b is vinyl; and

R^d is ethyl.

259. The compound of any one of claims 255 to 258, or a salt thereof, wherein M is 2H.

260. The compound of any one of claims 255 to 258, or a salt thereof, wherein M is a metal species selected from the group consisting of Cu(II), Co(II), Fe(II), Mn(II), Mg(II), Zn(II), Pd(II), Sn(IV), Al(III), Pt(II), Si(IV), Ge(IV), Ga(III) and In(III).

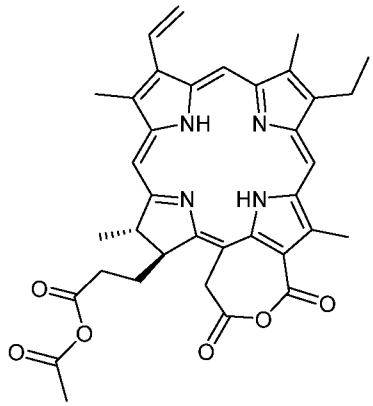
261. The compound of claim 255, that is:



,

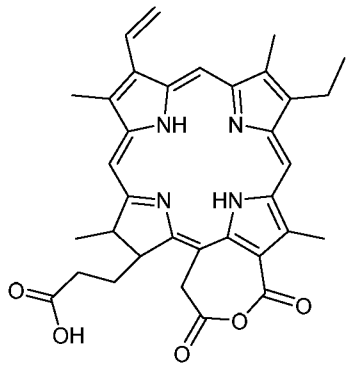
or a salt thereof.

262. The compound of claim 255, that is:



or a salt thereof.

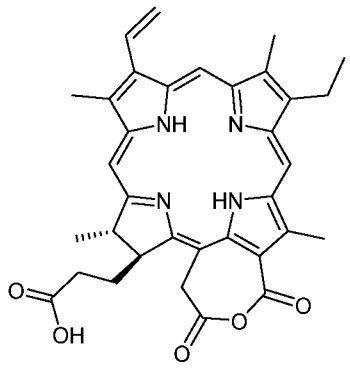
263. The compound of claim 255, that is:



,

or a salt thereof.

264. The compound of claim 255, that is:



,

or a salt thereof.

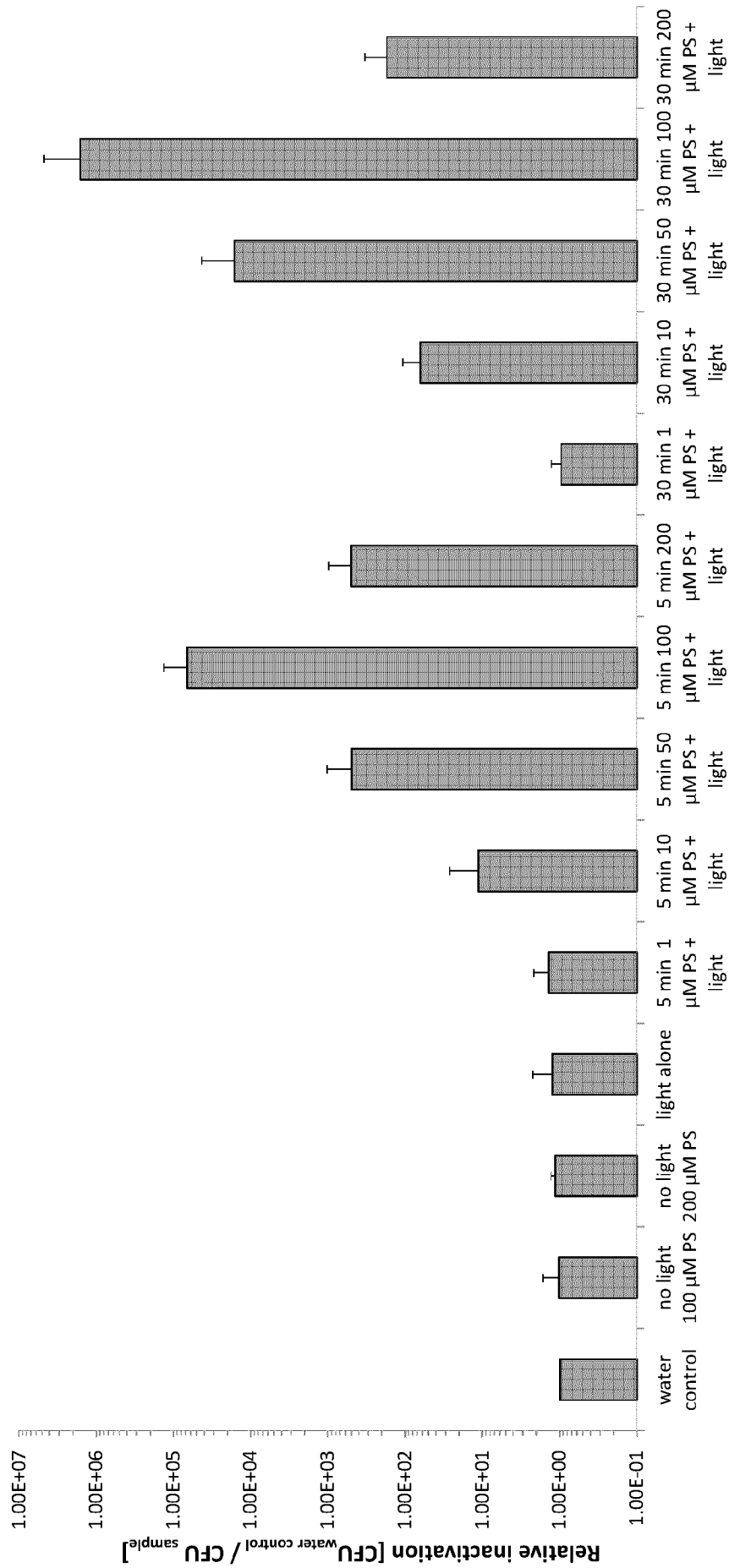

Relative inactivation [CFU water control / CFU sample]
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
water control
no light 100 µM PS
no light 200 µM PS
light alone
5 min 1 µM PS + light
5 min 10 µM PS + light
5 min 50 µM PS + light
5 min 100 µM PS + light
5 min 200 µM PS + light
30 min 1 µM PS + light
30 min 10 µM PS + light
30 min 50 µM PS + light
30 min 100 µM PS + light
30 min 200 µM PS + light

Figure 1

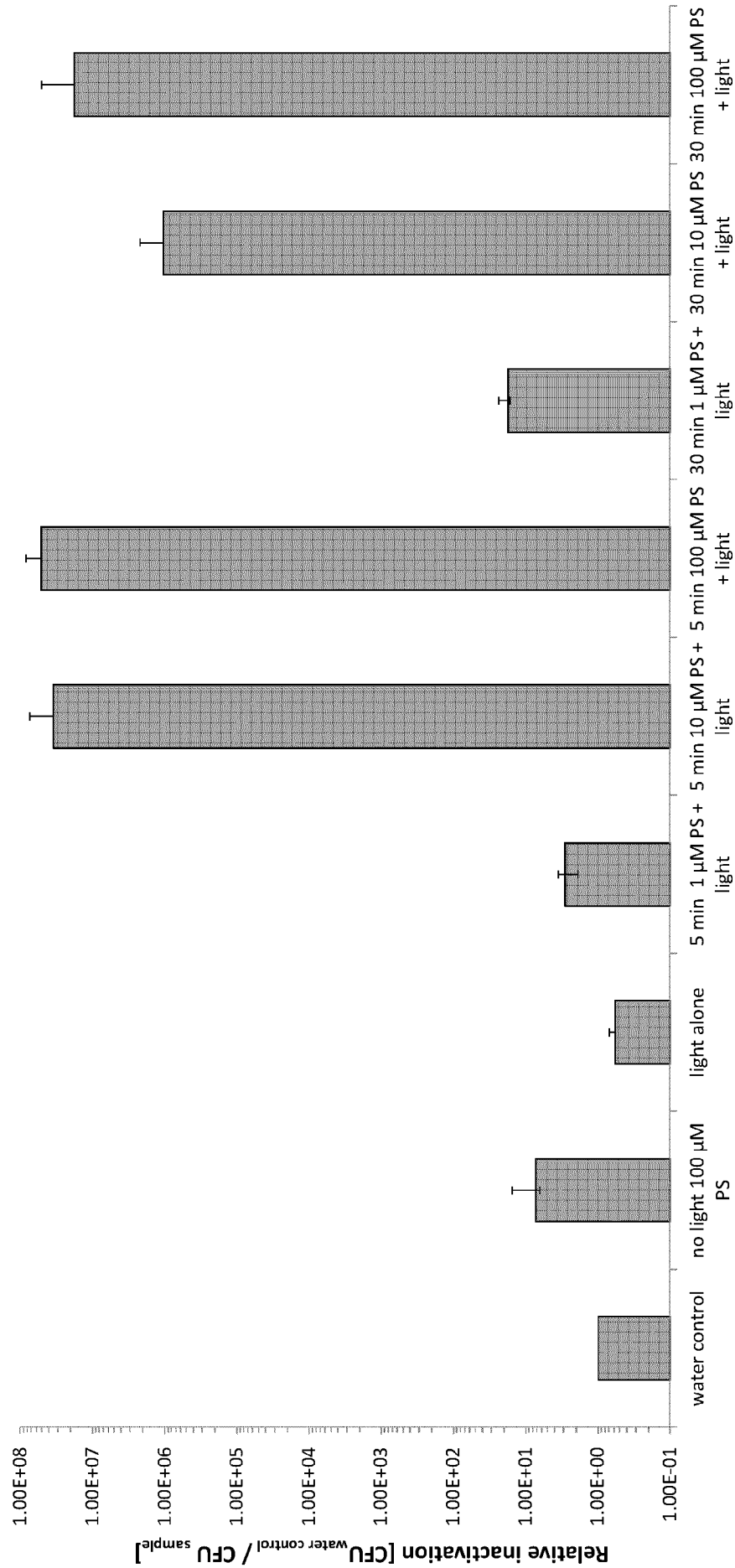

Relative inactivation [CFU water control / CFU sample]
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
water control
no light 100 µM PS
light alone
5 min 1 µM PS + light
5 min 10 µM PS + light
5 min 100 µM PS + light
30 min 1 µM PS + light
30 min 10 µM PS + light
30 min 100 µM PS + light

Figure 2

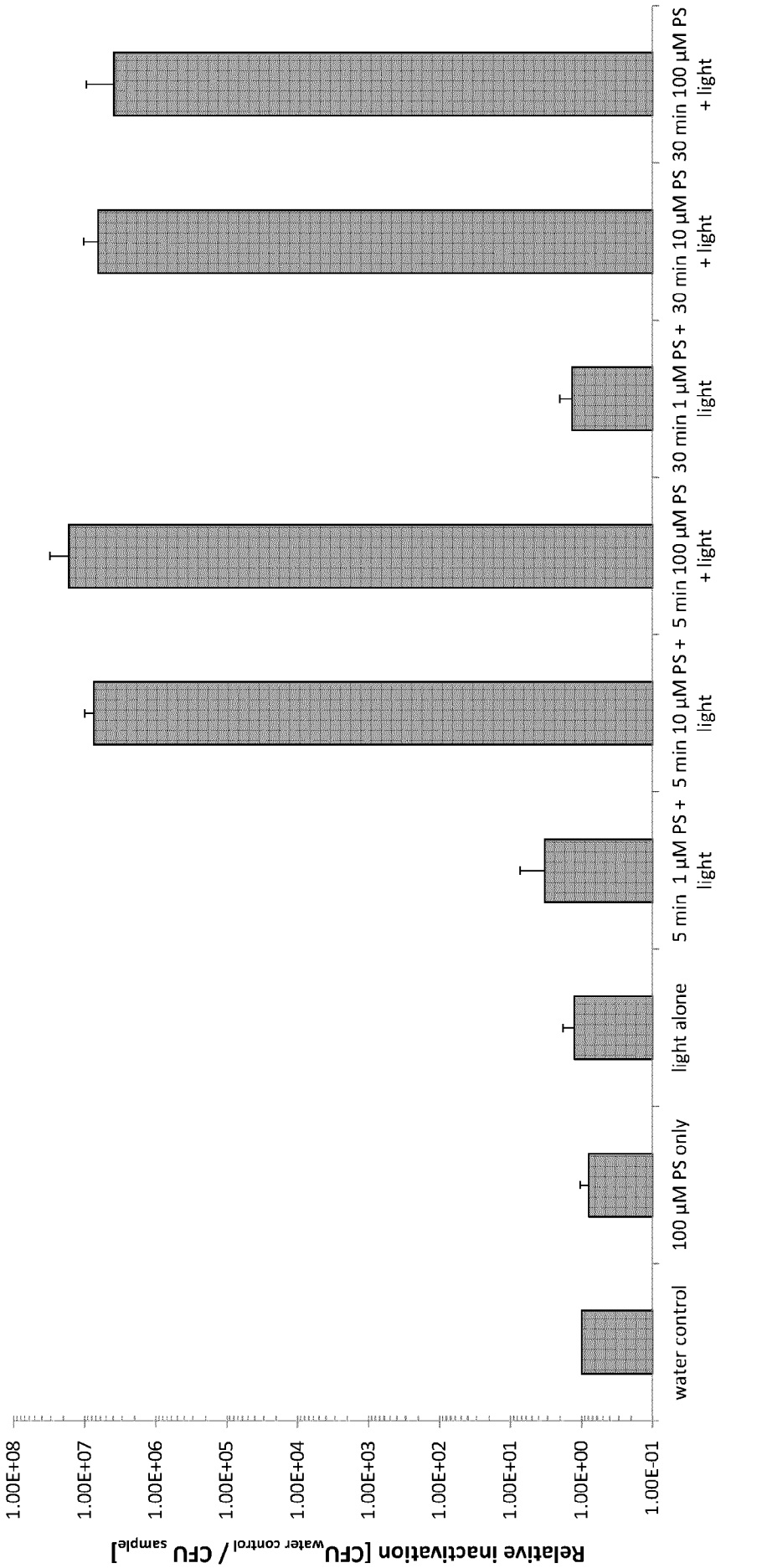

Relative inactivation [CFU water control / CFU sample]
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
water control
100 µM PS only
light alone
5 min 1 µM PS + light
5 min 10 µM PS + light
5 min 100 µM PS + light
30 min 1 µM PS + light
30 min 10 µM PS + light
30 min 100 µM PS + light

Figure 3

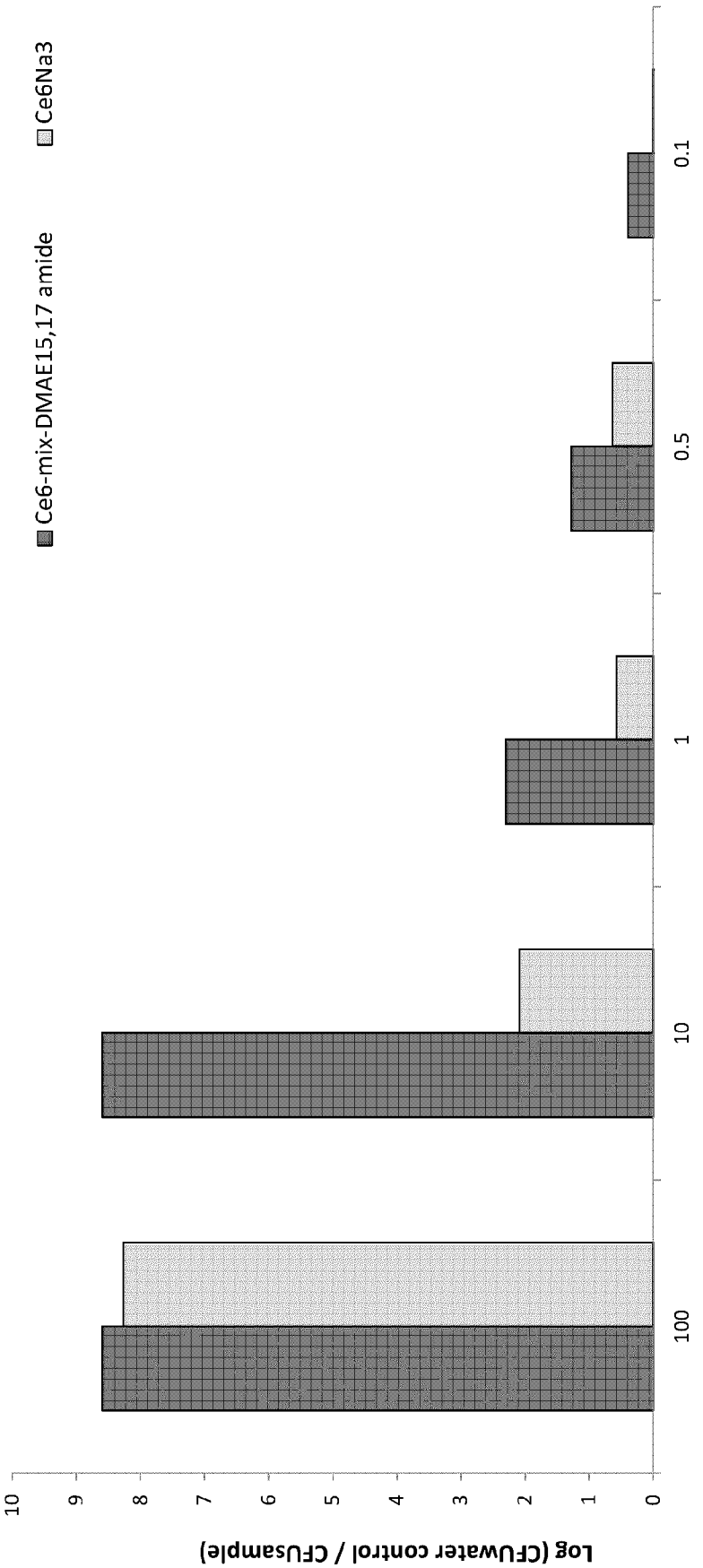

Ce6-mix-DMAE15,17 amide
Ce6Na3
Log (CFUwater control / CFUsample)
0
1
2
3
4
5
6
7
8
9
10
Concentration (uM)
100
10
1
0.5
0.1

Figure 4

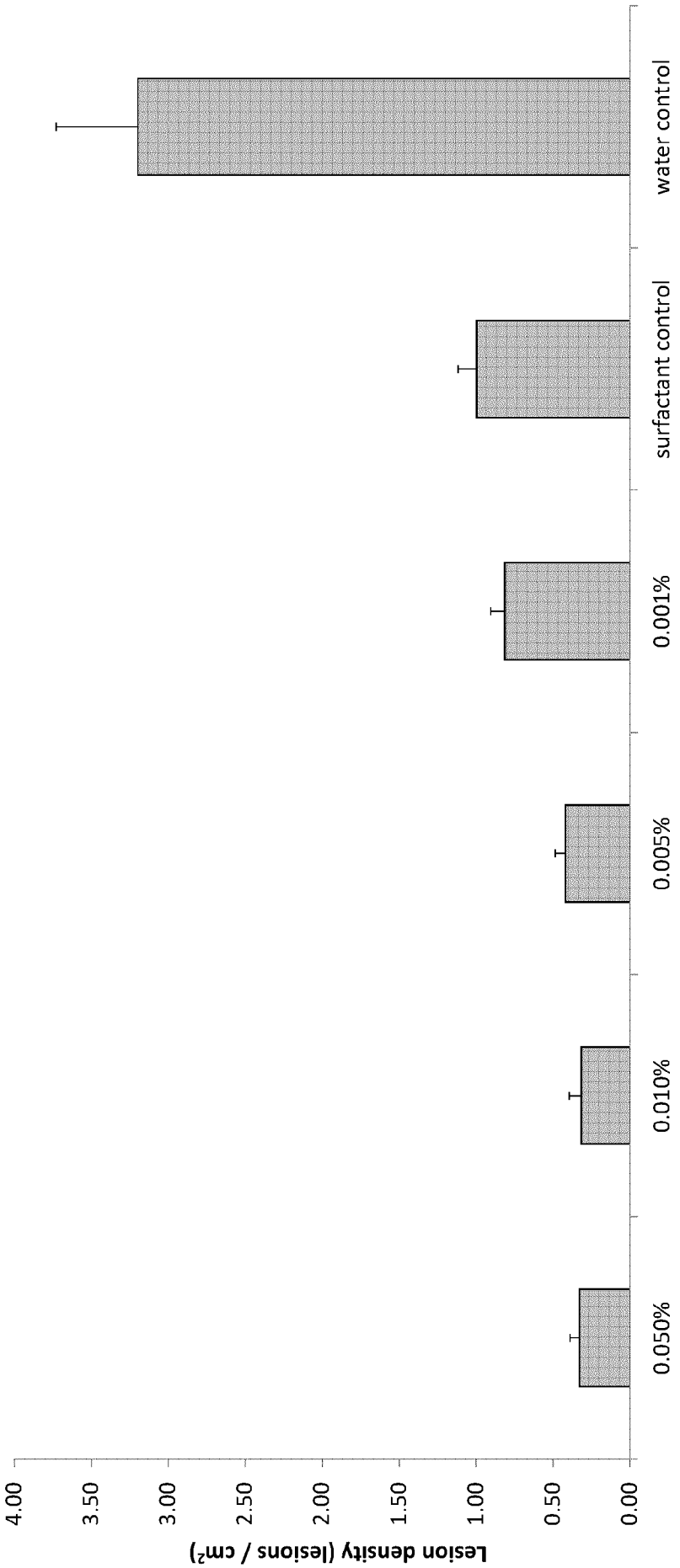

Lesion density (lesions / cm²)
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0.050%
0.010%
0.005%
0.001%
surfactant control
water control
Ce6-mix-DMAE15,17 amide concentration (wt %)

Figure 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2020/050083

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***C07D 487/22*** (2006.01) , ***A01N 3/00*** (2006.01) , ***A01N 43/90*** (2006.01) , ***A01N 59/16*** (2006.01) , ***A01N 59/20*** (2006.01) , ***A01P 1/00*** (2006.01) (more IPCs on the last page)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC: ***C07D 487/22*** (2006.01) , ***A01N 3/00*** (2006.01) , ***A01N 43/90*** (2006.01) , ***A01N 59/16*** (2006.01) , ***A01N 59/20*** (2006.01) , ***A01P 1/00*** (2006.01), ***A01P 21/00*** (2006.01) , ***A01P 3/00*** (2006.01) , ***A01P 7/04*** (2006.01)

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Canadian Patent Database; Questel Orbit; STN

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2018135882 (NA, K et AL) 26 July 2018 (26-07-2018)	1-6, 10-13, 15-17, 20-22, 25-27, 199
X	GUO, X et AL, "- *Synergistic antiproliferative effect of chemo-phototherapy: Synthesis and photodynamic activity evaluation of novel Chlorin e6-artesunate conjugates as antiproliferative*	1-6, 10-13, 15-17, 20-22, 25-27, 199
Y	*agents*". Bioorganic & Medicinal Chemistry Letters, 2017, Vol. 27(19), pp. 4548-4551,	200-241
X	WO 2009137062 (HASAN, T et AL) 12 November 2009 (12-11-2009)	1-6, 10-13, 15-17, 20-22, 25-27, 199
X	WO 2013192521 (HASAN, T et AL) 27 December 2013 (27-12-2013)	1-6, 10-13, 15-17, 20-22, 25-27, 199
Y		200-241
X	CN 107417706 (GUO, X et AL) 1 December 2017 (01-12-2017) (abstract)	1-6, 10-13. 15-17, 20-22, 25-27, 29-31

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

☑ See patent family annex.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	
"D" document cited by the applicant in the international application	
"E" earlier application or patent but published on or after the international filing date	
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	
	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
	"&" document member of the same patent family

Date of the actual completion of the international search 17 March 2020 (17-03-2020)	Date of mailing of the international search report 22 April 2020 (22-04-2020)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 819-953-2476	Authorized officer Marcel Beaudoin (819) 639-6968

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2020/050083

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
WO2018135882A1	26 July 2018 (26-07-2018)	WO2018135882A1	26 July 2018 (26-07-2018)
		KR20180085689A	27 July 2018 (27-07-2018)
		KR102007278B1	06 August 2019 (06-08-2019)
WO2009137062A2	12 November 2009 (12-11-2009)	WO2009137062A2	12 November 2009 (12-11-2009)
		WO2009137062A3	30 December 2009 (30-12-2009)
		EP2285381A2	23 February 2011 (23-02-2011)
		EP2285381A4	09 January 2013 (09-01-2013)
		EP2285381B1	16 December 2015 (16-12-2015)
		EP3056497A1	17 August 2016 (17-08-2016)
		EP3056497B1	29 August 2018 (29-08-2018)
		ES2699376T3	11 February 2019 (11-02-2019)
		US2011112059A1	12 May 2011 (12-05-2011)
		US9828622B2	28 November 2017 (28-11-2017)
		US2018094292A1	05 April 2018 (05-04-2018)
WO2013192521A1	27 December 2013 (27-12-2013)	WO2013192521A1	27 December 2013 (27-12-2013)
		US2016073634A1	17 March 2016 (17-03-2016)
CN107417706A	01 December 2017 (01-12-2017)	CN107417706A	01 December 2017 (01-12-2017)
		CN107417706B	16 July 2019 (16-07-2019)

A01P 21/00 (2006.01) , ***A01P 3/00*** (2006.01) , ***A01P 7/04*** (2006.01)