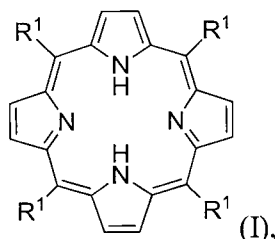


Claims:

1. A method for synthesizing a substituted porphyrin having the formula:

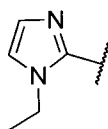


wherein R¹ is substituted or unsubstituted imidazolyl, said method comprising:

- (i) contacting a pyrrole with an R¹-substituted aldehyde, wherein said contacting is performed in a solvent system comprising a positive azeotrope;
- (ii) allowing said pyrrole to react with said R¹-substituted aldehyde in said solvent system under azeotropic distillation conditions, thereby forming a substituted-porphyrinogen; and
- (iii) oxidizing said substituted-porphyrinogen, thereby synthesizing a substituted porphyrin having formula (I).

2. The method of claim 1, wherein said contacting is performed using about one equivalent pyrrole and about one equivalent R¹-substituted aldehyde.

3. The method of claim **Error! Reference source not found.**1, wherein R¹ is:



4. The method of claim 1, wherein said solvent system comprises a first solvent and an acid.

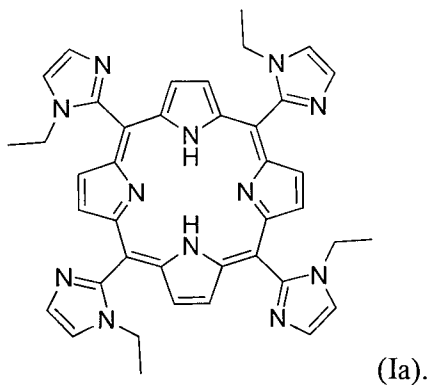
5. The method of claim 4, wherein said first solvent is chlorobenzene, *m*-xylene, or toluene.

6. The method of claim 5, wherein said first solvent is toluene.

7. The method of claim 4, wherein said acid is a carboxylic acid.

8. The method of claim 7, wherein said carboxylic acid is acetic acid, formic acid, propionic acid, valeric acid or butyric acid.
9. The method of claim 8, wherein said carboxylic acid is propionic acid.
10. The method of claim 1, wherein said positive azeotrope comprises water and toluene.
11. The method of claim 1, wherein said substituted porphyrin has a yield of from about 10% to about 35%.
12. The method of claim 11, wherein said substituted porphyrin has a yield of at least about 20%.
13. The method of claim 1, wherein said reacting is performed at a temperature from about 40 °C to about 150 °C.
14. The method of claim 13, wherein said reacting is performed at a temperature of about 140 °C.
15. The method of claim 1, wherein said oxidizing is performed by exposure to air or by using an oxidant.
16. The method of claim 15, wherein said oxidant is 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.
17. The method of claim 1, wherein said oxidizing is performed in a low oxygen environment.
18. The method of claim 17, wherein said oxidizing is performed in the absence of an exogenous oxidant.

19. The method of claim 1, wherein the compound of formula (I) has the formula:

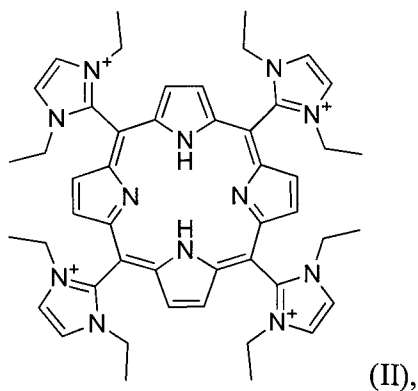


20. The method of claim 1, wherein said method further comprises contacting the compound of formula (I) or formula (Ia) with a metal salt.

21. The method of claim 20, wherein said metal salt is a transition metal salt.

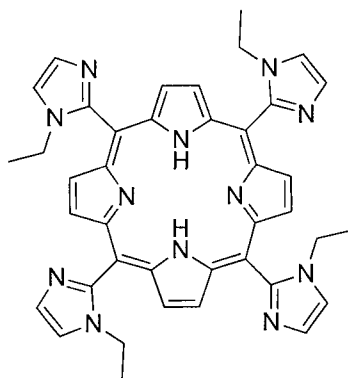
22. The method of claim 21, wherein said metal salt is a manganese salt.

23. A method for synthesizing a compound of formula



said method comprising:

contacting with an ethylating agent a compound having the formula



(Ia),

thereby synthesizing a compound of formula (II),

wherein said method further comprises:

- (i) contacting about one equivalent of a pyrrole with about one equivalent of 1-ethyl-1*H*-imidazole-2-carbaldehyde, wherein said contacting is performed in a solvent comprising a positive azeotrope;
- (ii) allowing said pyrrole to react with said 1-ethyl-1*H*-imidazole-2-carbaldehyde, in said solvent under azeotropic distillation conditions, thereby forming a substituted-porphyrinogen; and
- (iii) oxidizing said substituted-porphyrinogen, thereby synthesizing the compound of formula (Ia).

24. The method of claim 23, further comprising a counterion selected from the group consisting of a halogen anion, SCN^- , HSO_4^- , SO_4^{2-} , $\text{H}_2\text{PO}_4^{-1}$, HPO_4^{2-} , PO_4^{3-} , NO_3^- , PF_6^- , or BF_4^- .

25. The method of claim 23, wherein said ethylating agent is alkyl-halogen.

26. The method of claim 25, wherein said alkyl-halogen is iodoethane.

27. The method of claim 25, wherein said contacting is performed at a temperature of about 100 °C.

28. The method of claim 23, wherein said ethylating agent is a Meerwein salt.

29. The method of claim 28, wherein said Meerwein salt is triethyloxonium tetrafluoroborate or triethyloxonium hexafluorophosphate.

30. The method of claim 29, wherein said contacting is performed at a temperature from about 50 °C to about 100 °C.

31. The method of claim 30, wherein said contacting is performed at a temperature of about 80 °C.

32. The method of claim 30, wherein said contacting is performed in dimethylformamide.

33. The method of claim 23, wherein said method further comprises precipitation of the compound having formula (II) with a precipitating agent.

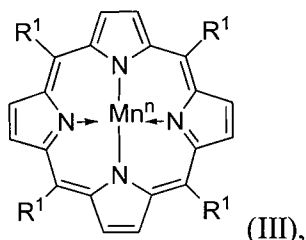
34. The method of claim 33, wherein said precipitating agent is an ammonium salt.

35. The method of claim 23, wherein said method further includes contacting the compound of formula (II) with a metal salt.

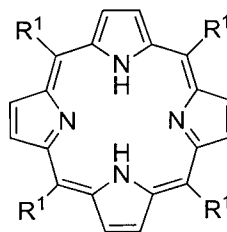
36. The method of claim 35, wherein said metal salt is a transition metal salt.

37. The method of claim 36, wherein said metal salt is a manganese salt.

38. A method for synthesizing a hydrate compound having the formula



wherein R¹ is substituted or unsubstituted imidazolyl; and n is 2 or 3, said method comprising:

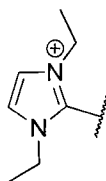


(i) contacting a compound of formula (I) with over about 2 equivalents of a Mn(III) salt in a solvent, thereby forming a reaction mixture;

(ii) heating said reaction mixture thereby synthesizing a compound of formula (III); and

(iii) hydrating said compound of formula (III) thereby forming a hydrate of compound (III).

39. The method of claim **Error! Reference source not found.**38, wherein R^1 is:



40. The method of claim 38, wherein n is 3.

41. The method of claim 38, wherein said compound of formula (I) is contacted with about 2 to about 10 equivalents of Mn(III) salt.

42. The method of claim 41, wherein said compound of formula (I) is contacted with about 2 to about 5 equivalents of Mn(III) salt.

43. The method of claim 42, wherein said compound of formula (I) is contacted with about 2 to about 3 equivalents of Mn(III) salt.

44. The method of claim 38, wherein said solvent is acetonitrile.

45. The method of claim 44, wherein said reaction mixture is heated to a temperature of about 15 °C to about 70 °C.

46. The method of claim 38, wherein said method further comprises filtering said reaction mixture.

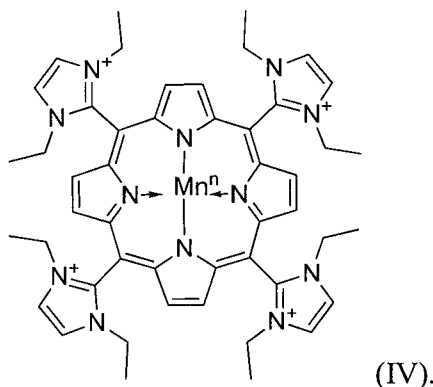
47. The method of claim 38, wherein said method further comprises allowing said reaction mixture to cool to a temperature of about 10 °C to about 30 °C.

48. The method of claim 38, wherein said hydrating comprises contacting compound of formula (III) with a gas having a relative humidity from about 30% to about 70%.

49. The method of claim 48, wherein said compound of formula (III) is dried after contacting with said gas.

50. The method of claim 38, wherein said method further comprises contacting said reaction mixture with an anion-exchanging agent and allowing said mixture to react with said anion-exchanging agent.

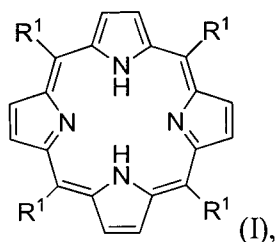
51. The method of synthesis of claim 38, wherein the compound has the formula:



52. The method of claim 51, further comprising a counterion selected from the group consisting of a halogen anion, SCN^- , HSO_4^- , SO_4^{2-} , $\text{H}_2\text{PO}_4^{-1}$, HPO_4^{2-} , PO_4^{3-} , NO_3^- , PF_6^- , or BF_4^- .

53. The method of claim 52, wherein n is 3.

54. A method for purifying a compound of formula:



wherein R^1 is substituted or unsubstituted imidazolyl, said method comprising:

(i) combining a compound of formula (I) and a purification solvent in a reaction vessel thereby forming a purification mixture, wherein said compound is insoluble in said purification solvent, wherein said purification solvent is 2-butanone, 1,4-dioxane, acetonitrile, or cyclohexanone;

(ii) heating said purification mixture;

(iii) cooling said purification mixture; and
(iv) filtering said purification mixture thereby purifying a compound of formula (I).

55. The method of claim **Error! Reference source not found.**54, wherein said purification solvent is 2-butanone.

56. The method of claim 54, wherein said purification mixture is heated to about 80 °C.

57. The method of claim 54 or 56, wherein said purification mixture is heated for about 1 hour.

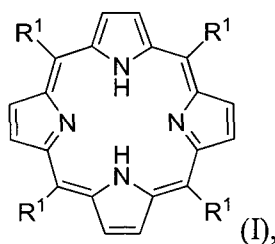
58. The method of claim 54, wherein said purification mixture is cooled to about 0 °C.

59. The method of claim 54 or 58, wherein said purification mixture is cooled for about 2 hours.

60. The method of claim 54, wherein said filtering comprises washing the filter cake comprising said compound with a washing solvent.

61. The method of claim 60, wherein said washing solvent comprises 2-butanone or tert-butyl methyl ether.

62. A method for purifying a compound having the formula:



Wherein, R¹ is substituted or unsubstituted imidazolyl, said method comprises:

- (i) dissolving a compound of formula (I) in a purifying solvent in a reaction vessel to form a purifying mixture, wherein said purifying solvent is dimethylformamide;
- (ii) heating said purifying mixture;
- (iii) cooling said purifying mixture; and
- (iv) drying said purifying mixture thereby purifying a compound of formula (I).

63. The method of claim 62, wherein said purifying mixture is heated to about 150 °C.
64. The method of claim 63, wherein said purifying mixture is heated for about 1 hour.
65. The method of claim 62, wherein said purifying mixture is cooled to about 25 °C.
66. The method of claim 62, wherein said purifying mixture is filtered following cooling.
67. The method of claim 66, wherein said filtering comprises washing the filter cake comprising said compound of formula (I) with dimethylformamide.