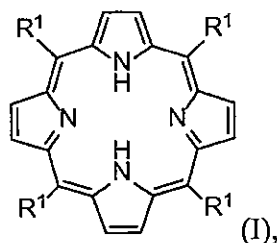


WHAT IS CLAIMED IS:

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



2
3 wherein R¹ is substituted or unsubstituted heterocycloalkyl or substituted or
4 unsubstituted heteroaryl, said method comprising:

5 (i) contacting a pyrrole with an R¹-substituted aldehyde, wherein said
6 contacting is performed in a solvent system comprising a positive azeotrope;

7 (ii) allowing said pyrrole to react with said R¹-substituted aldehyde in said
8 solvent system under azeotropic distillation conditions, thereby forming a substituted-
9 porphyrinogen; and

10 (iii) oxidizing said substituted-porphyrinogen, thereby synthesizing a
11 substituted porphyrin having formula (I).

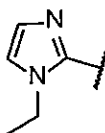
1 2. The method of claim 1, wherein said contacting is performed using
2 about one equivalent pyrrole and about one equivalent R¹-substituted aldehyde.

1 3. The method of claim 1, wherein R¹ is substituted or unsubstituted
2 heteroaryl.

1 4. The method of claim 3, wherein R¹ is substituted or unsubstituted
2 imidazolyl, substituted or unsubstituted pyrazolyl, substituted or unsubstituted thiazolyl, or
3 substituted or unsubstituted triazolyl.

1 5. The method of claim 4, wherein R¹ is substituted imidazolyl.

1 6. The method of claim 5, wherein R¹ is:



- 1 7. The method of claim 1, wherein R¹ is substituted or unsubstituted
2 heteroaryl.
- 1 8. The method of claim 7, wherein R¹ is substituted or unsubstituted
2 pyridinyl, substituted or unsubstituted pyrazinyl, substituted or unsubstituted pyrimidinyl, or
3 substituted or unsubstituted pyridazinyl.
- 1 9. The method of claim 1, wherein said solvent system comprises a first
2 solvent and an acid.
- 1 10. The method of claim 9, wherein said first solvent is chlorobenzene, *m*-
2 xylene, or toluene.
- 1 11. The method of claim 10, wherein said first solvent is toluene.
- 1 12. The method of claim 9, wherein said acid is a carboxylic acid.
- 1 13. The method of claim 12, wherein said carboxylic acid is acetic acid,
2 formic acid, propionic acid, valeric acid or butyric acid.
- 1 14. The method of claim 13, wherein said carboxylic acid is propionic
2 acid.
- 1 15. The method of claim 1, wherein said positive azeotrope comprises
2 water and toluene.
- 1 16. The method of claim 1, wherein said substituted porphyrin has a yield
2 of from about 6% to about 35%.
- 1 17. The method of claim 1, wherein said substituted porphyrin has a yield
2 of from about 8% to about 35%.
- 1 18. The method of claim 1, wherein said substituted porphyrin has a yield
2 of from about 10% to about 35%.
- 1 19. The method of claim 18, wherein said substituted porphyrin has a yield
2 of at least about 10%.

1 20. The method of claim 18, wherein said substituted porphyrin has a yield
2 of at least about 15%.

1 21. The method of claim 18, wherein said substituted porphyrin has a yield
2 of at least about 20%.

1 22. The method of claim 18, wherein said substituted porphyrin has a yield
2 of at least about 25%.

1 23. The method of claim 18, wherein said substituted porphyrin has a yield
2 of at least about 30%.

1 24. The method of claim 1, wherein said reacting is performed at a
2 temperature from about 40 °C to about 150 °C.

1 25. The method of claim 24, wherein said reacting is performed at a
2 temperature of about 140 °C.

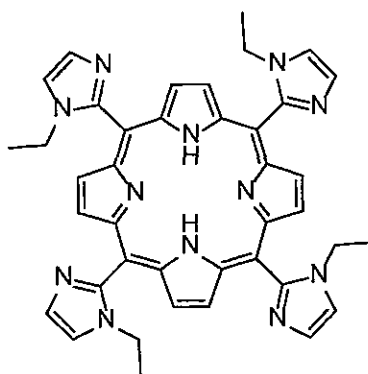
1 26. The method of claim 1, wherein said oxidizing is performed by
2 exposure to air or by using an oxidant.

1 27. The method of claim 26, wherein said oxidant is 2,3-dichloro-5,6-
2 dicyano-1,4-benzoquinone.

1 28. The method of claim 1, wherein said oxidizing is performed in a low
2 oxygen environment.

1 29. The method of claim 28, wherein said oxidizing is performed in the
2 absence of an exogenous oxidant.

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



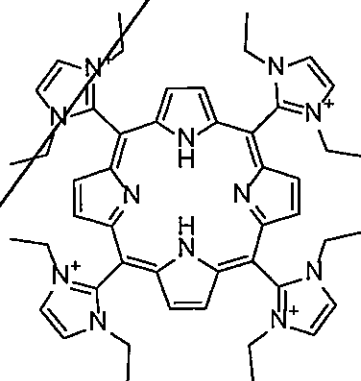
(Ia).

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

- 1 32. The method of claim 31, wherein said metal salt is a transition metal
2 salt.

- 1 33. The method of claim 32, wherein said metal salt is a manganese salt.

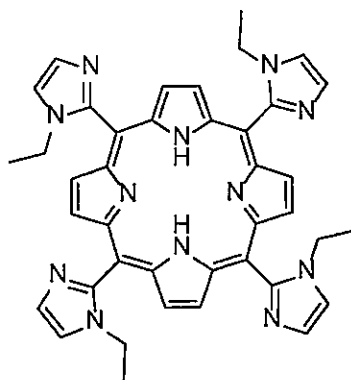
- 1 34. A method for synthesizing a compound of formula



(II),

2 said method comprising:

3 contacting with an ethylating agent a compound having the formula



(Ia),

thereby synthesizing a compound of formula (II).

35. The method of claim 34, 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^- .

36. The method of claim 34, 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 a substituted porphyrin having formula (Ia).

37. The method of claim 34, wherein said ethylating agent is alkyl-halogen.

38. The method of claim 37, wherein said alkyl-halogen is iodoethane.

39. The method of claim 37, wherein said contacting is performed at a temperature of about 100 °C.

40. The method of claim 34, wherein said ethylating agent is a Meerwein salt.

41. The method of claim 40, wherein said Meerwein salt is triethyloxonium tetrafluoroborate or triethyloxonium hexafluorophosphate.

42. The method of claim 41, wherein said contacting is performed at a temperature from about 50 °C to about 100 °C.

43. The method of claim 42, wherein said contacting is performed at a temperature of about 80 °C.

44. The method of claim 42, wherein said contacting is performed in dimethylformamide.

45. The method of claim 34, wherein said method further comprises precipitation of the compound having formula (II) with a precipitating agent.

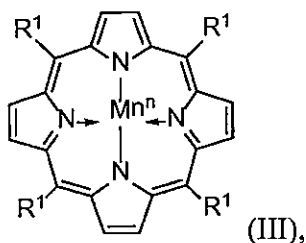
46. The method of claim 45, wherein said precipitating agent is an ammonium salt.

47. The method of claim 34, wherein said method further includes contacting the compound of formula (II) with a metal salt.

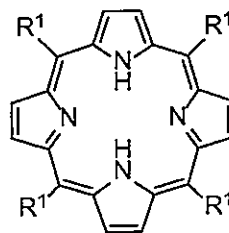
48. The method of claim 47, wherein said metal salt is a transition metal salt.

49. The method of claim 48, wherein said metal salt is a manganese salt.

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



wherein R^1 is substituted or unsubstituted heterocycloalkyl or substituted or unsubstituted heteroaryl; 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;

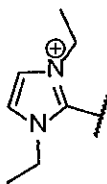
(ii) heating said reaction mixture thereby synthesizing a compound of formula (III); and

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

51. The method of claim 50, wherein R^1 is substituted or unsubstituted imidazolyl, substituted or unsubstituted pyrazolyl, substituted or unsubstituted thiazolyl, or substituted or unsubstituted triazolyl.

52. The method of claim 51, wherein R^1 is substituted imidazolyl.

53. The method of claim 52, wherein R^1 is:



54. The method of claim 50, wherein R^1 is substituted or unsubstituted heteroaryl.

55. The method of claim 54, wherein R^1 is substituted or unsubstituted pyridinyl, substituted or unsubstituted pyrazinyl, substituted or unsubstituted pyrimidinyl, or substituted or unsubstituted pyridazinyl.

56. The method of claim 50, wherein n is 3.

57. The method of claim 50, wherein said compound of formula (I) is contacted with about 2 to about 10 equivalents of Mn(III) salt.

58. The method of claim 57, wherein said compound of formula (I) is contacted with about 2 to about 5 equivalents of Mn(III) salt.

59. The method of claim 58, wherein said compound of formula (I) is contacted with about 2 to about 3 equivalents of Mn(III) salt.

60. The method of claim 50, wherein said solvent is acetonitrile.

1 61. The method of claim 60, wherein said reaction mixture is heated to a
2 temperature of about 15 °C to about 70 °C.

1 62. The method of claim 50, wherein said method further comprises
2 filtering said reaction mixture.

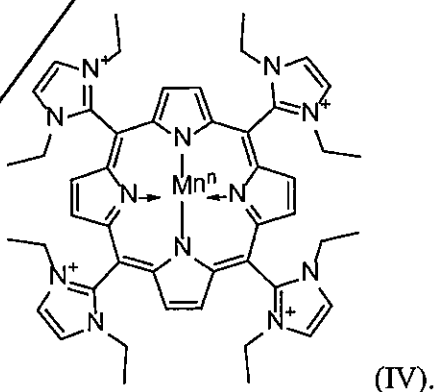
1 63. The method of claim 50, wherein said method further comprises
2 allowing said reaction mixture to cool to a temperature of about 10 °C to about 30 °C.

1 64. The method of claim 50, wherein said hydrating comprises contacting
2 compound of formula (III) with a gas having a relative humidity from about 30% to about
3 70%.

1 65. The method of claim 64, wherein said compound of formula (III) is
2 dried after contacting with said gas.

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

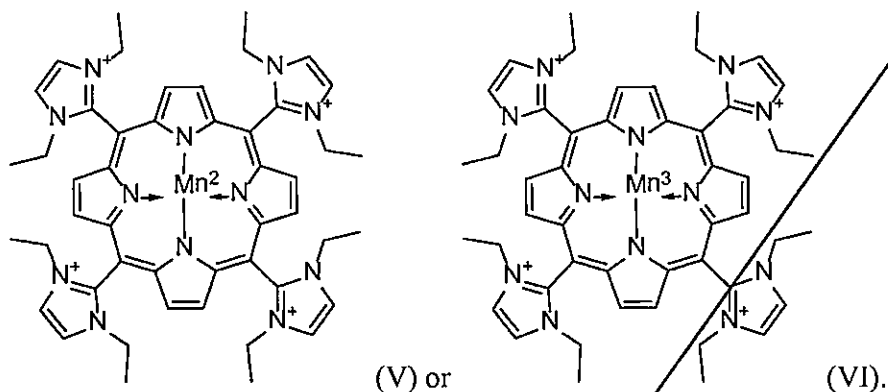
1 67. The method of synthesis of claim 50, wherein the compound has the
2 formula:



1 68. The method of claim 67, further comprising a counterion selected from
2 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^- ,
3 PF_6^- , or BF_4^- .

1 69. The method of claim 68, wherein n is 3.

70. A container comprising a plurality compounds, wherein said plurality of compounds have the formula:



71. The container of claim 70, wherein at least 60% of said plurality of compounds have formula (VI).

72. The container of claim 70, wherein at least 90% of said plurality of compounds have formula (VI).

73. The container of claim 70, wherein at least 95% of said plurality of compounds have formula (VI).

74. The container of claim 70, further comprising a counterion selected from the group consisting of a halogen anion, SCN^- , HSO_4^- , SO_4^{2-} , $H_2PO_4^{-1}$, HPO_4^{-2} , PO_4^{-3} , NO_3^- , PF_6^- , or BF_4^- .

75. The container of any one of claims 70 to 74, wherein said plurality of compounds is in water thereby forming a pharmaceutical formulation.

76. The container of claim 75, wherein said pharmaceutical formulation is at a pH of from about 3.5 to about 7.0.

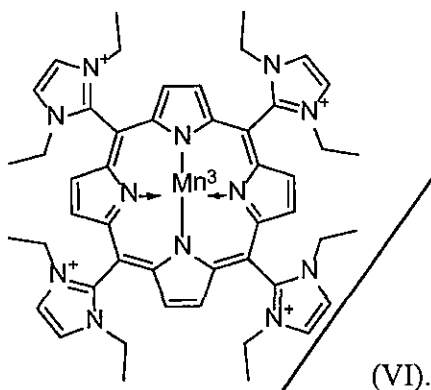
77. The container of claim 75 or 76, wherein said pharmaceutical formulation consists essentially of water and the compound of claim 70.

78. The container of claim 75 or 76, wherein said pharmaceutical formulation consists of water, the compound of claim 70, and pH adjustment ions.

1 79. The container of claim 75 or 76, wherein the pharmaceutical
2 formulation does not comprise a buffer.

1 80. The container of claim 75 or 76, wherein the pharmaceutical
2 formulation does not comprise a pharmaceutical excipient.

1 81. A pharmaceutical formulation comprising water and a compound
2 having the formula:



1 82. The pharmaceutical formulation of claim 81, wherein the formulation
2 comprises less than 10% Mn(II).

1 83. The pharmaceutical formulation of claim 81, wherein the formulation
2 comprises less than 5% Mn(II).

1 84. The pharmaceutical formulation of claim 81, wherein the formulation
2 comprises less than 1% Mn(II).

1 85. The pharmaceutical formulation of claim 81 at a pH of from about 3.5
2 to about 7.0.

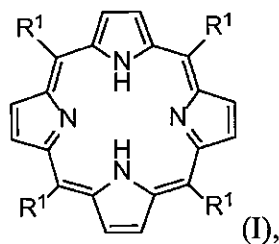
1 86. The pharmaceutical formulation of claim 81 or 85 consisting
2 essentially of water and said compound.

1 87. The pharmaceutical formulation of claim 81 or 85 consisting of water,
2 the compound, and pH adjustment ions.

1 88. The pharmaceutical formulation of claim 81 or 85, wherein the
2 pharmaceutical formulation does not comprise a buffer.

1 89. The pharmaceutical formulation of claim 81 or 85, wherein the
2 pharmaceutical formulation does not comprise a pharmaceutical excipient.

1 90. A method for purifying a compound of formula:



2
3 said method comprising:

4 (i) combining a compound of formula (I) and a purification solvent in a
5 reaction vessel thereby forming a purification mixture, wherein said compound is insoluble in
6 said purification solvent;

7 (ii) heating said purification mixture;

8 (iii) cooling said purification mixture; and

9 (iv) filtering said purification mixture thereby purifying a compound of
10 formula (I).

1 91. The method of claim 90, wherein said purification solvent is 2-
2 butanone, 1,4-dioxane, acetonitrile, ethyl acetate or cyclohexanone.

1 92. The method of claim 91, wherein said purification solvent is 2-
2 butanone.

1 93. The method of claim 90, wherein said purification mixture is heated to
2 about 80 °C.

1 94. The method of claim 90 or 93, wherein said purification mixture is
2 heated for about 1 hour.

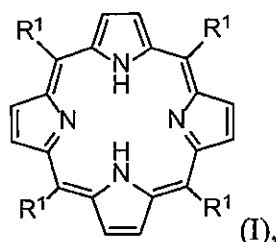
1 95. The method of claim 90, wherein said purification mixture is cooled to
2 about 0 °C.

1 96. The method of claim 90 or 95, wherein said purification mixture is
2 cooled for about 2 hours.

1 97. The method of claim 90, wherein said filtering comprises washing the
2 filter cake comprising said compound with a washing solvent.

1 98. The method of claim 97, wherein said washing solvent comprises 2-
2 butanone or tert-butyl methyl ether.

1 99. A method for purifying a compound having the formula:



2
3 wherein, said method comprises:

- 4 (i) dissolving a compound of formula (I) in a purifying solvent in a reaction
5 vessel to form a purifying mixture;
6 (ii) heating said purifying mixture;
7 (iii) cooling said purifying mixture; and
8 (iv) drying said purifying mixture thereby purifying a compound of formula (I).

1 100. The method of claim 99, wherein said purifying solvent is
2 dimethylformamide.

1 101. The method of claim 99, wherein said purifying mixture is heated to
2 about 150 °C.

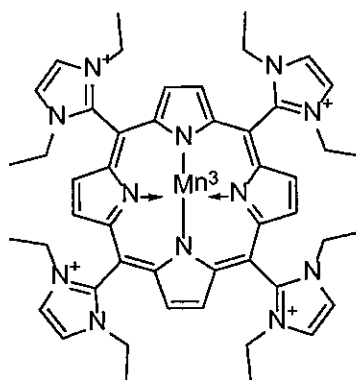
1 102. The method of claim 101, wherein said purifying mixture is heated for
2 about 1 hour.

1 103. The method of claim 99, wherein said purifying mixture is cooled to
2 about 25 °C.

1 104. The method of claim 99, wherein said purifying mixture is filtered
2 following cooling.

1 105. The method of claim 104, wherein said filtering comprises washing the
2 filter cake comprising said compound of formula (I) with dimethylformamide.

1 106. A crystal comprising a compound having the formula:



(VI)

1 107. The crystal of claim 106, wherein the crystal is a hydrate.

1 108. A crystalline form of [5,10,15,20-tetrakis(1,3-diethylimidazolium-2-yl)porphyrinato]manganese(III) chloride hydrate complex characterized by an x-ray powder
2 diffraction spectrum, said x-ray powder diffraction spectrum comprising angle 2θ peaks at
3 about 6.9 ± 0.2 , 8.2 ± 0.2 , 9.5 ± 0.2 , 11.4 ± 0.2 , 12.8 ± 0.2 , 14.5 ± 0.2 , 15.0 ± 0.2 , 16.1 ± 0.2 ,
4 16.3 ± 0.2 , 18.1 ± 0.2 , 20.3 ± 0.2 , 23.5 ± 0.2 , 24.8 ± 0.2 , 25.6 ± 0.2 , 26.5 ± 0.2 , and 29.2 ± 0.2 ,
5 wherein said an x-ray powder diffraction spectrum is obtained using a Cu K α
6 radiation source ($1.54 \text{ \AA}$).
7

1 109. The crystalline form of 108, wherein said x-ray powder diffraction
2 spectrum further comprises angle 2θ peaks at about 13.8 ± 0.2 , 17.4 ± 0.2 , 19.0 ± 0.2 , $19.4 \pm$
3 0.2 , 20.7 ± 0.2 , 21.1 ± 0.2 , 21.5 ± 0.2 , 22.0 ± 0.2 , 22.5 ± 0.2 , 22.8 ± 0.2 , 26.9 ± 0.2 , 27.6 ± 0.2 ,
4 28.5 ± 0.2 , 30.2 ± 0.2 , 30.5 ± 0.2 , 31.2 ± 0.2 , 37.3 ± 0.2 , 38.5 ± 0.2 , and 41.1 ± 0.2 .

1 110. A crystalline form of [5,10,15,20-tetrakis(1,3-diethylimidazolium-2-yl)porphyrinato]manganese(III) chloride hydrate complex characterized by an x-ray powder
2 diffraction spectrum, said x-ray powder diffraction spectrum comprising d spacings at about
3 12.85 , 10.82 , 9.28 , 7.78 , 6.91 , 6.11 , 5.91 , 5.49 , 5.42 , 4.89 , 4.37 , 3.78 , 3.58 , 3.47 , 3.36 , and
4 3.06 ,
5 wherein said an x-ray powder diffraction spectrum is obtained using a Cu K α
6 radiation source ($1.54 \text{ \AA}$).
7

111. The crystalline form of claim 110, wherein said x-ray powder diffraction spectrum further comprises d spacings at about, 7.57, 6.44, 5.10, 4.67, 4.58, 4.29, 4.2, 4.13, 4.05, 3.96, 3.89, 3.31, 3.22, 3.13, 2.96, 2.93, 2.86, 2.41, 2.34, and 2.19.

112. A crystalline form of [5,10,15,20-tetrakis(1,3-diethylimidazolium-2-yl)porphyrinato]manganese(III) chloride hydrate complex characterized by an x-ray powder diffraction spectrum, said x-ray powder diffraction spectrum comprising angle 2θ peaks at about 26.2 ± 0.2 , 22.9 ± 0.2 , 20.0 ± 0.2 , 18.6 ± 0.2 , 15.2 ± 0.2 , 13.7 ± 0.2 , 13.5 ± 0.2 , 13.0 ± 0.2 , 12.4 ± 0.2 , 11.4 ± 0.2 , 10.6 ± 0.2 , 8.9 ± 0.2 , 6.8 ± 0.2 , and 6.0 ± 0.2 , wherein said an x-ray powder diffraction spectrum is obtained using a Cu K α radiation source (1.54 Å).

113. The crystalline form of 112, wherein said x-ray powder diffraction spectrum further comprises angle 2θ peaks at about 29.4 ± 0.2 , 28.5 ± 0.2 , 27.5 ± 0.2 , 27.0 ± 0.2 , 25.7 ± 0.2 , 25.2 ± 0.2 , 23.7 ± 0.2 , 17.8 ± 0.2 , 17.1 ± 0.2 , 14.6 ± 0.2 , 10.9 ± 0.2 , 9.9 ± 0.2 , and 8.2 ± 0.2 .

114. A crystalline form of [5,10,15,20-tetrakis(1,3-diethylimidazolium-2-yl)porphyrinato]manganese(III) chloride hydrate complex characterized by an x-ray powder diffraction spectrum, said x-ray powder diffraction spectrum comprising d spacings at about 14.74, 12.93, 9.99, 8.34, 7.74, 7.14, 6.80, 6.55, 6.45, 5.83, 4.78, 4.43, 3.89, and 3.40, wherein said an x-ray powder diffraction spectrum is obtained using a Cu K α radiation source (1.54 Å).

115. The crystalline form of claim 114, wherein said x-ray powder diffraction spectrum further comprises d spacings at about 10.82, 8.90, 8.10, 6.05, 5.19, 4.98, 3.75, 3.54, 3.47, 3.30, 3.24, 3.13, and 3.04.

116. A crystalline form of [5,10,15,20-tetrakis(1,3-diethylimidazolium-2-yl)porphyrinato]manganese(III) chloride hydrate complex characterized by an x-ray powder diffraction spectrum, said x-ray powder diffraction spectrum comprising angle 2θ peaks at about 27.7 ± 0.2 , 26.6 ± 0.2 , 19.9 ± 0.2 , 15.4 ± 0.2 , 14.7 ± 0.2 , 11.6 ± 0.2 , 10.1 ± 0.2 , 8.6 ± 0.2 , and 6.9 ± 0.2 , wherein said an x-ray powder diffraction spectrum is obtained using a Cu K α radiation source (1.54 Å).

117. The crystalline form of 116, wherein said x-ray powder diffraction spectrum further comprises angle 2θ peaks at about 29.6 ± 0.2 , 25.7 ± 0.2 , 23.4 ± 0.2 , 20.4 ± 0.2 , and 13.7 ± 0.2 .

118. A crystalline form of [5,10,15,20-tetrakis(1,3-diethylimidazolium-2-yl)porphyrinato]manganese(III) chloride hydrate complex characterized by an x-ray powder diffraction spectrum, said x-ray powder diffraction spectrum comprising d spacings at about 12.89, 10.27, 8.79, 7.60, 6.04, 5.74, 4.45, 3.35, and 3.22,

wherein said an x-ray powder diffraction spectrum is obtained using a Cu K α radiation source (1.54 Å).

119. The crystalline form of claim 118, wherein said x-ray powder diffraction spectrum further comprises d spacings at about 6.45, 4.35, 3.80, 3.46, and 3.02.

120. A crystalline form of [5,10,15,20-tetrakis(1,3-diethylimidazolium-2-yl)porphyrinato]manganese(III) chloride hydrate complex characterized by an x-ray powder diffraction spectrum, said x-ray powder diffraction spectrum comprising angle 2θ peaks at about 29.5 ± 0.2 , 27.3 ± 0.2 , 26.3 ± 0.2 , 24.7 ± 0.2 , 23.5 ± 0.2 , 22.5 ± 0.2 , 21.6 ± 0.2 , 20.5 ± 0.2 , 19.3 ± 0.2 , 17.7 ± 0.2 , 13.1 ± 0.2 , 10.8 ± 0.2 , 9.9 ± 0.2 , 8.5 ± 0.2 , and 6.0 ± 0.2 ,

wherein said an x-ray powder diffraction spectrum is obtained using a Cu K α radiation source (1.54 Å).

121. The crystalline form of 120, wherein said x-ray powder diffraction spectrum further comprises angle 2θ peaks at about 32.6 ± 0.2 , 19.8 ± 0.2 , 18.6 ± 0.2 , and 14.8 ± 0.2 .

122. A crystalline form of [5,10,15,20-tetrakis(1,3-diethylimidazolium-2-yl)porphyrinato]manganese(III) chloride hydrate complex characterized by an x-ray powder diffraction spectrum, said x-ray powder diffraction spectrum comprising angle 2θ peaks at about 23.5 ± 0.2 , 9.1 ± 0.2 , 6.9 ± 0.2 , and 5.8 ± 0.2 ,

wherein said an x-ray powder diffraction spectrum is obtained using a Cu K α radiation source (1.54 Å).

123. The crystalline form of 122, wherein said x-ray powder diffraction spectrum further comprises angle 2θ peaks at about 27.5 ± 0.2 , 24.6 ± 0.2 , 18.2 ± 0.2 , 13.9 ± 0.2 , 13.0 ± 0.2 , 11.7 ± 0.2 , and 7.9 ± 0.2 .

124. A crystalline form of [5,10,15,20-tetrakis(1,3-diethylimidazolium-2-yl)porphyrinato]manganese(III) chloride hydrate complex characterized by an x-ray powder diffraction spectrum, said x-ray powder diffraction spectrum comprising d spacings at about 15.12, 12.74, 9.75, and 3.78,

wherein said an x-ray powder diffraction spectrum is obtained using a Cu K α radiation source (1.54 Å).

125. The crystalline form of claim 124, wherein said x-ray powder diffraction spectrum further comprises d spacings at about 11.14, 7.55, 6.81, 6.36, 4.87, 3.62, and 3.24.

126. A crystalline form of [5,10,15,20-tetrakis(1,3-diethylimidazolium-2-yl)porphyrinato]manganese(III) chloride hydrate complex characterized by an x-ray powder diffraction spectrum, said x-ray powder diffraction spectrum comprising angle 2θ peaks at about 27.7 ± 0.2 , 23.6 ± 0.2 , 23.1 ± 0.2 , 20.7 ± 0.2 , 6.9 ± 0.2 , and 5.8 ± 0.2 ,

wherein said an x-ray powder diffraction spectrum is obtained using a Cu K α radiation source (1.54 Å).

127. The crystalline form of 126, wherein said x-ray powder diffraction spectrum further comprises angle 2θ peaks at about 29.2 ± 0.2 , 28.9 ± 0.2 , 27.1 ± 0.2 , 26.5 ± 0.2 , 26.2 ± 0.2 , 24.8 ± 0.2 , 22.4 ± 0.2 , 22.2 ± 0.2 , 21.5 ± 0.2 , 20.3 ± 0.2 , 18.1 ± 0.2 , 17.3 ± 0.2 , 16.3 ± 0.2 , 14.9 ± 0.2 , 13.8 ± 0.2 , 11.5 ± 0.2 , and 9.2 ± 0.2 .

128. A crystalline form of [5,10,15,20-tetrakis(1,3-diethylimidazolium-2-yl)porphyrinato]manganese(III) chloride hydrate complex characterized by an x-ray powder diffraction spectrum, said x-ray powder diffraction spectrum comprising angle 2θ peaks at about 27.7 ± 0.2 , 20.7 ± 0.2 , 13.8 ± 0.2 , 11.4 ± 0.2 , 9.5 ± 0.2 , 8.2 ± 0.2 , and 6.9 ± 0.2 ,

wherein said an x-ray powder diffraction spectrum is obtained using a Cu K α radiation source (1.54 Å).

1 129. The crystalline form of 128, wherein said x-ray powder diffraction
2 spectrum further comprises angle 2θ peaks at about 23.5 ± 0.2 , 22.8 ± 0.2 , 16.3 ± 0.2 , and $5.9 \pm$
3 0.2 .

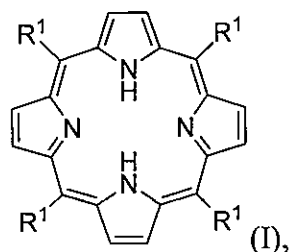
1 130. A crystalline form of [5,10,15,20-tetrakis(1,3-diethylimidazolium-2-
2 yl)porphyrinato]manganese(III) chloride hydrate complex characterized by an x-ray powder
3 diffraction spectrum, said x-ray powder diffraction spectrum comprising d spacings at about
4 12.84 , 10.83 , 9.26 , 7.77 , 6.43 , 4.29 , and 3.22 ,

5 wherein said an x-ray powder diffraction spectrum is obtained using a Cu $K\alpha$
6 radiation source ($1.54 \text{ \AA}$).

1 131. The crystalline form of claim 130, wherein said x-ray powder
2 diffraction spectrum further comprises d spacings at about 15.07 , 12.84 , 10.83 , 9.26 , 7.77 ,
3 6.43 , 5.42 , 4.29 , 3.89 , 3.79 , and 3.22 .

Claims:

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



wherein R¹ is substituted or unsubstituted heterocycloalkyl or substituted or unsubstituted heteroaryl, 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).

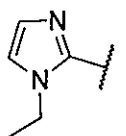
2. The method of claim 1, wherein said contacting is performed using about one equivalent pyrrole and about one equivalent R¹-substituted aldehyde.

3. The method of claim 1, wherein R¹ is substituted or unsubstituted heteroaryl.

4. The method of claim 3, wherein R¹ is substituted or unsubstituted imidazolyl, substituted or unsubstituted pyrazolyl, substituted or unsubstituted thiazolyl, or substituted or unsubstituted triazolyl.

5. The method of claim 4, wherein R¹ is substituted imidazolyl.

6. The method of claim 5, wherein R¹ is:



7. The method of claim 1, wherein R¹ is substituted or unsubstituted heteroaryl.
8. The method of claim 7, wherein R¹ is substituted or unsubstituted pyridinyl, substituted or unsubstituted pyrazinyl, substituted or unsubstituted pyrimidinyl, or substituted or unsubstituted pyridazinyl.
9. The method of claim 1, wherein said solvent system comprises a first solvent and an acid.
10. The method of claim 9, wherein said first solvent is chlorobenzene, *m*-xylene, or toluene.
11. The method of claim 10, wherein said first solvent is toluene.
12. The method of claim 9, wherein said acid is a carboxylic acid.
13. The method of claim 12, wherein said carboxylic acid is acetic acid, formic acid, propionic acid, valeric acid or butyric acid.
14. The method of claim 13, wherein said carboxylic acid is propionic acid.
15. The method of claim 1, wherein said positive azeotrope comprises water and toluene.
16. The method of claim 1, wherein said substituted porphyrin has a yield of from about 6% to about 35%.
17. The method of claim 1, wherein said substituted porphyrin has a yield of from about 8% to about 35%.
18. The method of claim 1, wherein said substituted porphyrin has a yield of from about 10% to about 35%.
19. The method of claim 18, wherein said substituted porphyrin has a yield of at least about 10%.

20. The method of claim 18, wherein said substituted porphyrin has a yield of at least about 15%.

21. The method of claim 18, wherein said substituted porphyrin has a yield of at least about 20%.

22. The method of claim 18, wherein said substituted porphyrin has a yield of at least about 25%.

23. The method of claim 18, wherein said substituted porphyrin has a yield of at least about 30%.

24. The method of claim 1, wherein said reacting is performed at a temperature from about 40 °C to about 150 °C.

25. The method of claim 24, wherein said reacting is performed at a temperature of about 140 °C.

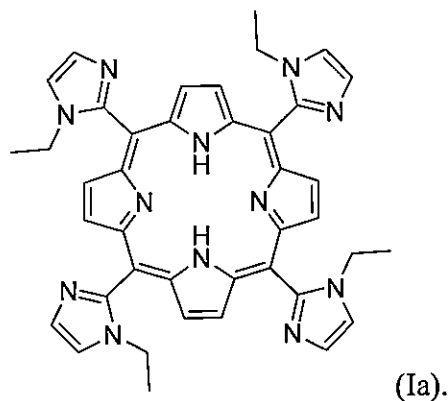
26. The method of claim 1, wherein said oxidizing is performed by exposure to air or by using an oxidant.

27. The method of claim 26, wherein said oxidant is 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

28. The method of claim 1, wherein said oxidizing is performed in a low oxygen environment.

29. The method of claim 28, wherein said oxidizing is performed in the absence of an exogenous oxidant.

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

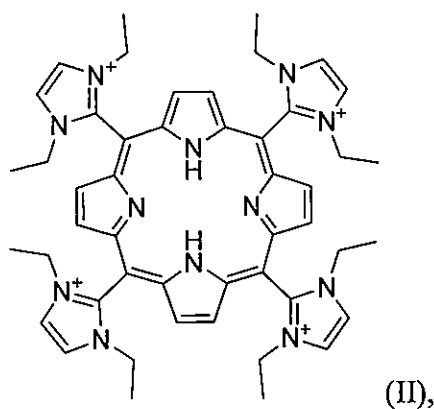


31. The method of claim 1, wherein said method further comprises contacting the compound of formula (I) or formula (Ia) with a metal salt.

32. The method of claim 31, wherein said metal salt is a transition metal salt.

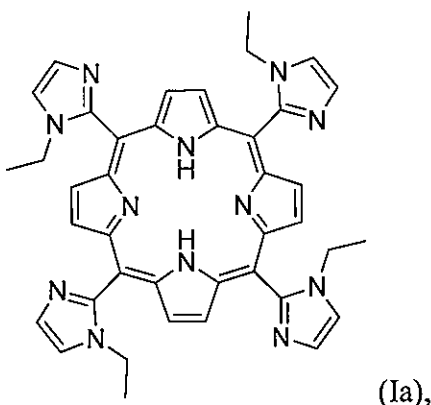
33. The method of claim 32, wherein said metal salt is a manganese salt.

34. A method for synthesizing a compound of formula



said method comprising:

contacting with an ethylating agent a compound having the formula



thereby synthesizing a compound of formula (II).

35. The method of claim 34, 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^- .

36. The method of claim 34, 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 a substituted porphyrin having formula (Ia).

37. The method of claim 34, wherein said ethylating agent is alkyl-halogen.

38. The method of claim 37, wherein said alkyl-halogen is iodoethane.

39. The method of claim 37, wherein said contacting is performed at a temperature of about 100 °C.

40. The method of claim 34, wherein said ethylating agent is a Meerwein salt.

41. The method of claim 40, wherein said Meerwein salt is triethyloxonium tetrafluoroborate or triethyloxonium hexafluorophosphate.

42. The method of claim 41, wherein said contacting is performed at a temperature from about 50 °C to about 100 °C.

43. The method of claim 42, wherein said contacting is performed at a temperature of about 80 °C.

44. The method of claim 42, wherein said contacting is performed in dimethylformamide.

45. The method of claim 34, wherein said method further comprises precipitation of the compound having formula (II) with a precipitating agent.

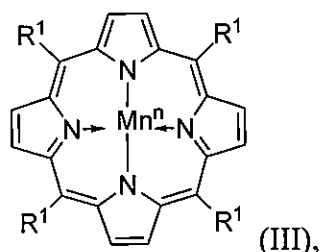
46. The method of claim 45, wherein said precipitating agent is an ammonium salt.

47. The method of claim 34, wherein said method further includes contacting the compound of formula (II) with a metal salt.

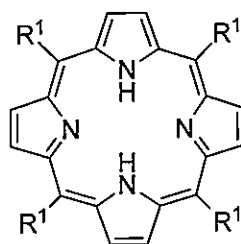
48. The method of claim 47, wherein said metal salt is a transition metal salt.

49. The method of claim 48, wherein said metal salt is a manganese salt.

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



wherein R¹ is substituted or unsubstituted heterocycloalkyl or substituted or unsubstituted heteroaryl; 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;

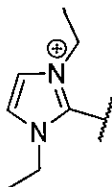
(ii) heating said reaction mixture thereby synthesizing a compound of formula (III); and

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

51. The method of claim 50, wherein R^1 is substituted or unsubstituted imidazolyl, substituted or unsubstituted pyrazolyl, substituted or unsubstituted thiazolyl, or substituted or unsubstituted triazolyl.

52. The method of claim 51, wherein R^1 is substituted imidazolyl.

53. The method of claim 52, wherein R^1 is:



54. The method of claim 50, wherein R^1 is substituted or unsubstituted heteroaryl.

55. The method of claim 54, wherein R^1 is substituted or unsubstituted pyridinyl, substituted or unsubstituted pyrazinyl, substituted or unsubstituted pyrimidinyl, or substituted or unsubstituted pyridazinyl.

56. The method of claim 50, wherein n is 3.

57. The method of claim 50, wherein said compound of formula (I) is contacted with about 2 to about 10 equivalents of Mn(III) salt.

58. The method of claim 57, wherein said compound of formula (I) is contacted with about 2 to about 5 equivalents of Mn(III) salt.

59. The method of claim 58, wherein said compound of formula (I) is contacted with about 2 to about 3 equivalents of Mn(III) salt.

60. The method of claim 50, wherein said solvent is acetonitrile.

61. The method of claim 60, wherein said reaction mixture is heated to a temperature of about 15 °C to about 70 °C.

62. The method of claim 50, wherein said method further comprises filtering said reaction mixture.

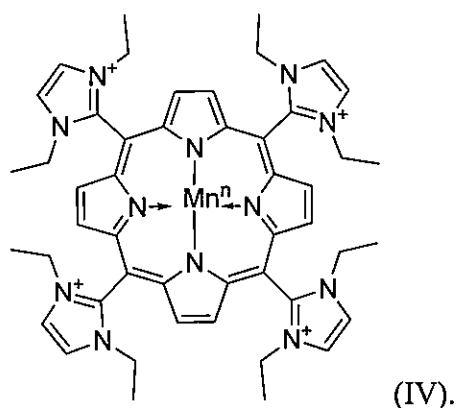
63. The method of claim 50, wherein said method further comprises allowing said reaction mixture to cool to a temperature of about 10 °C to about 30 °C.

64. The method of claim 50, wherein said hydrating comprises contacting compound of formula (III) with a gas having a relative humidity from about 30% to about 70%.

65. The method of claim 64, wherein said compound of formula (III) is dried after contacting with said gas.

66. The method of claim 50, 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.

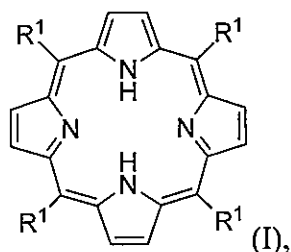
67. The method of synthesis of claim 50, wherein the compound has the formula:



68. The method of claim 67, 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^- .

69. The method of claim 68, wherein n is 3.

70. A method for purifying a compound of formula:



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;

(ii) heating said purification mixture;

(iii) cooling said purification mixture; and

(iv) filtering said purification mixture thereby purifying a compound of formula (I).

71. The method of claim 70, wherein said purification solvent is 2-butanone, 1,4-dioxane, acetonitrile, ethyl acetate or cyclohexanone.

72. The method of claim 71, wherein said purification solvent is 2-butanone.

73. The method of claim 70, wherein said purification mixture is heated to about 80 °C.

74. The method of claim 70 or 73, wherein said purification mixture is heated for about 1 hour.

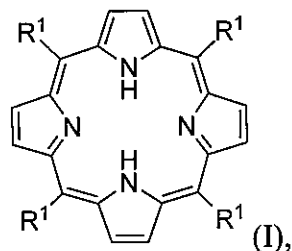
75. The method of claim 70, wherein said purification mixture is cooled to about 0 °C.

76. The method of claim 70 or 75, wherein said purification mixture is cooled for about 2 hours.

77. The method of claim 70, wherein said filtering comprises washing the filter cake comprising said compound with a washing solvent.

78. The method of claim 77, wherein said washing solvent comprises 2-butanone or tert-butyl methyl ether.

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



wherein, said method comprises:

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

80. The method of claim 79, wherein said purifying solvent is dimethylformamide.

81. The method of claim 79, wherein said purifying mixture is heated to about 150 °C.

82. The method of claim 81, wherein said purifying mixture is heated for about 1 hour.

83. The method of claim 79, wherein said purifying mixture is cooled to about 25 °C.

84. The method of claim 79, wherein said purifying mixture is filtered following cooling.

85. The method of claim 84, wherein said filtering comprises washing the filter cake comprising said compound of formula (I) with dimethylformamide.