Supplementary Materials: Zinc Porphyrins Possessing Three *p*-Carboxyphenyl Groups: Effect of the Donor Strength of Push-Groups on the Efficiency of Dye-Sensitized Solar Cells

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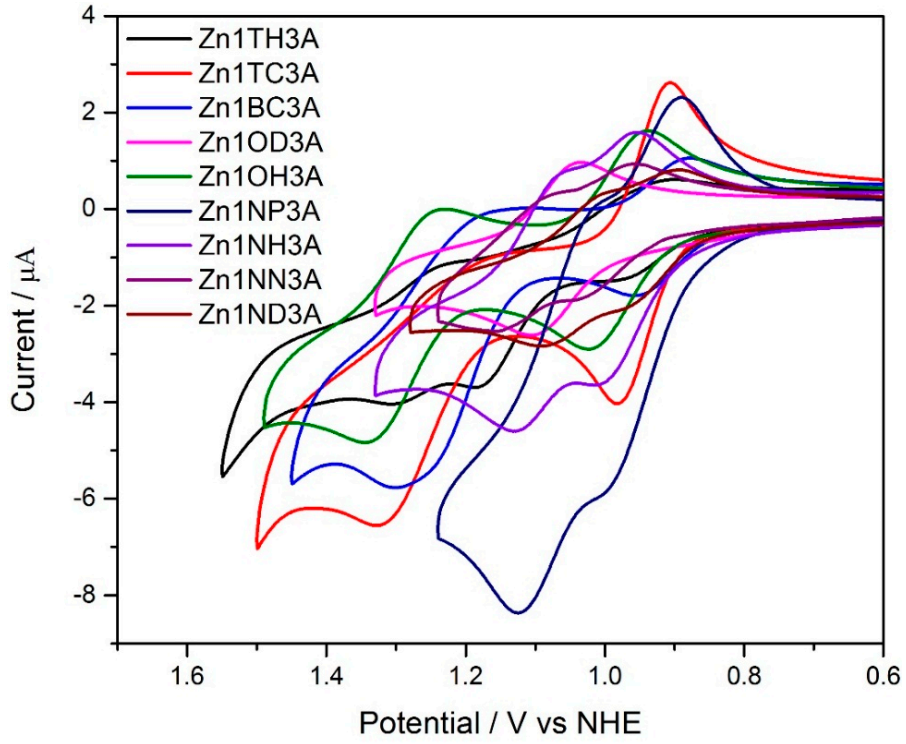


Figure S1. Cyclic voltamograms of studied porphyrins ZN_1TH_3A, Zn_1TC_3A, Zn_1BC_3A, Zn_1OD_3A, Zn_1OH_3A, Zn_1NP_3A, Zn_1NH_3A, Zn_1NN_3A and Zn_1NN_3A.

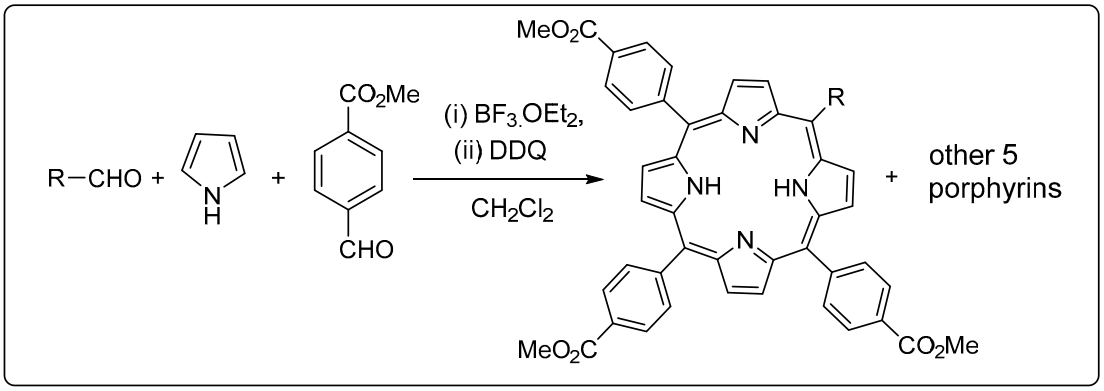
1. Synthesis of 1D-π-3A Porphyrin Sensitizers.

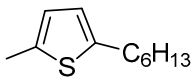
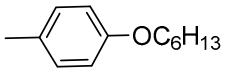
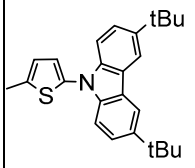
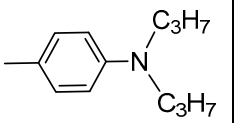
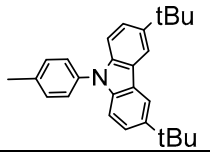
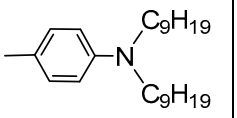
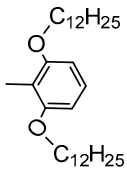
The zinc porphyrins used in this study Zn_1TH_3A, Zn_1TC_3A, Zn_1BC_3A, Zn_1OD_3A, Zn_1OH_3A, Zn_1NP_3A, Zn_1NH_3A, Zn_1NN_3A, and Zn_1ND_3A were synthesized in three steps: (I) mixed condensation; (II) zinc metalation; and (III) base hydrolysis. The synthesis and characterization data of Zn_1NH_3A and Zn_1ND_3A is reported elsewhere. For detail synthetic procedures please follow our previous articles.

1.1. Mixed Condensation

Condensation of pyrrole, methyl 4-formylbenzoate, and the required aldehyde under Lindsey's conditions catalyzed by boron trifluoride-diethyl etherate followed by subsequent oxidation by DDQ afforded the triester derivatives of porphyrins in good yield along with mixture of five other porphyrins. The yields of the triester derivatives porphyrins 1TH3E, 1TC3E, 1BC3E, 1OD3E, 1OH3E, 1NP3E, and 1NN3E obtained from each separate reaction are reported in Table S1.

Table S1. Mixed condensation.

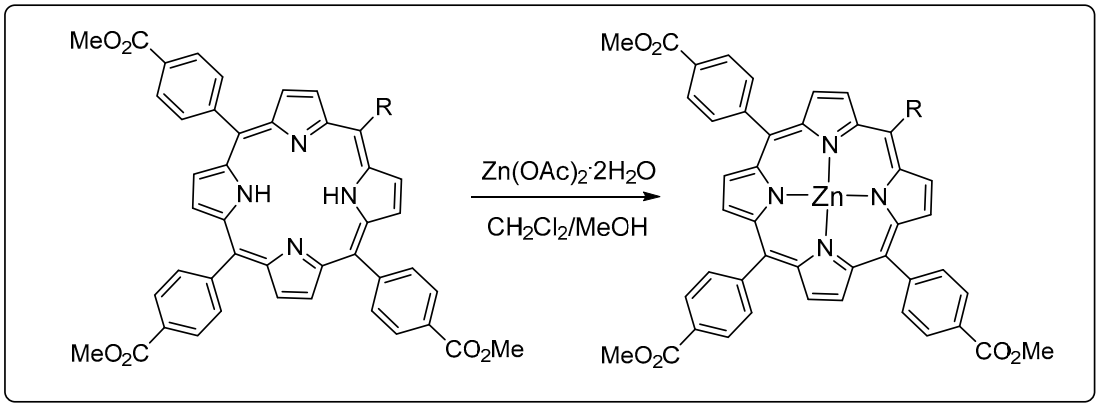


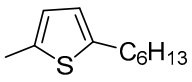
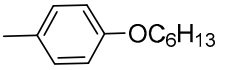
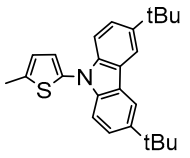
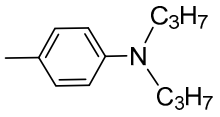
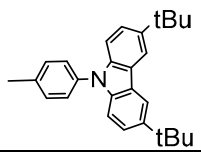
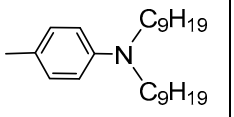
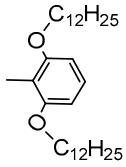
Product	R	Yield(%)	Product	R	Yield(%)
1TH3E		2.26	1OH3E		5.43
1TC3E		4.96	1NP3E		6.65
1BC3E		5.31	1NN3E		3.50
1OD3E		5.72			

1.2. Zn Metalation

The subsequent step of zinc metalation has been readily achieved in high yields by reacting free base porphyrin with zinc acetate. The yields of the zinc(II) porphyrins Zn_1TH_3E, Zn_1TC_3E, Zn_1BC_3E, Zn_1OD_3E, Zn_1OH_3E, Zn_1NP_3E, and Zn_1NN_3E are listed in Table S2. The success of zinc metalation of all the porphyrin was confirmed through the complete disappearance of the NMR resonance of inner NH with slight upfield shifts for all remaining protons. In ultraviolet visible (UV/Vis) spectra the zinc porphyrins shows single strong Soret band and two moderate Q bands.

Table S2. Zn metalation.

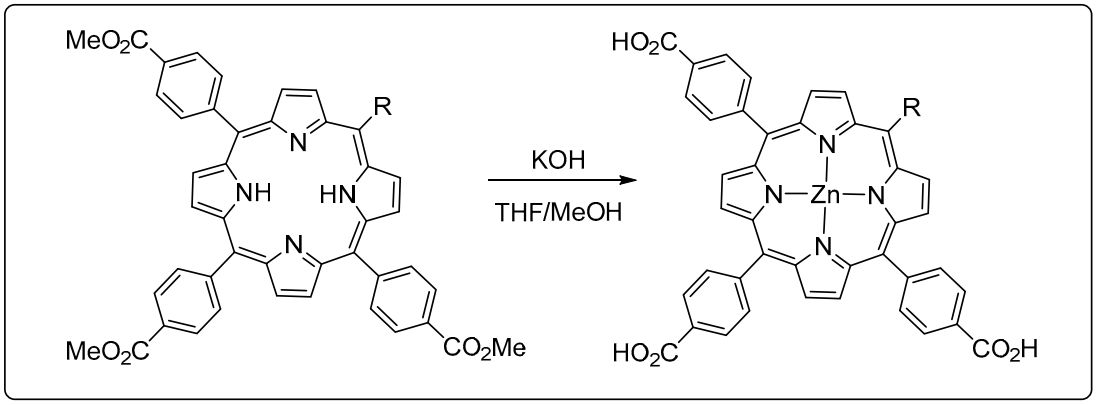


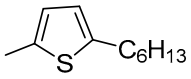
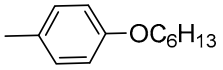
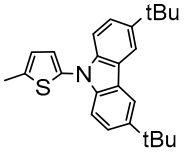
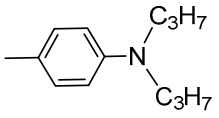
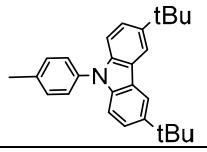
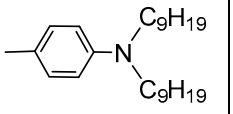
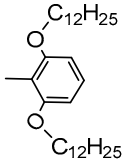
Product	R	Yield(%)	Product	R	Yield(%)
Zn1TH3E		83	Zn1OH3E		81
Zn1TC3E		97	Zn1NP3E		87
Zn1BC3E		97	Zn1NN3E		93
Zn1OD3E		90			

1.3. Hydrolysis

Hydrolysis of metal complexes has been achieved straightforwardly by reacting metal complexes in a mixture solution of THF and methanol with excess aqueous KOH. The yields of final hydrolyzed products Zn_1TH_3A, Zn_1TC_3A, Zn_1BC_3A, Zn_1OD_3A, Zn_1OH_3A, Zn_1NP_3A, and Zn_1NN_3A are listed in Table S3. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) spectra of final acid products show shifting of carbonyl peaks in the range of 1675−1700 cm^{-1} because of intermolecular hydrogen bonding. All of the porphyrins were fully characterized by optical spectroscopy, ATR-FTIR, nuclear magnetic resonance spectroscopy, and high-resolution mass spectrometry.

Table S3. Hydrolysis.



Dye	R	Yield(%)	Dye	R	Yield(%)
Zn1TH3A		99	Zn1OH3A		98
Zn1TC3A		90	Zn1NP3A		99
Zn1BC3A		93	Zn1NN3A		97
Zn1OD3A		98			

2. Syntheses and Characterization Data

5,10,15-tris(4-methoxycarbonylphenyl)20-(4-hexyl-2-thienyl)porphyrin (1TH3E). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.17 (d, *J* = 4.12 Hz, 2H), 8.79 (m, 6H), 8.44 (d, *J* = 7.7 Hz, 6H), 8.29 (d, *J* = 7.7 Hz, 6H), 7.71 (d, *J* = 3.2 Hz, 1H), 7.17 (d, *J* = 3.3 Hz, 1H), 4.11 (s, 9H), 3.12 (t, *J* = 7.6 Hz, 2H), 1.95 (*p*, *J* = 7.4 Hz, 2H), 1.61–1.59 (m, 2H), 1.48–1.40 (m, 4 H), 0.97 (t, *J* = 6.3 Hz, 3H), −2.73 (s, 2H); IR (Neat, cm^{-1}): 3315, 1719, 1606, 1434, 1270, 1177, 1099, 979, 962, 950, 796; λ_{abs}/nm (CH_2Cl_2): 422, 518, 556, 594, 648; HRMS-ESI calcd for $C_{54}H_{46}N_4O_6S$ ($[M+H]^+$): 879.3216, found 879.3269.

5,10,15-tris(4-methoxycarbonylphenyl)20-(3,6-di-tert-butyl-9-(thiophen-2-yl)-9H-carbazole)porphyrin (1TC3E). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.33 (d, *J* = 4.8 Hz, 2H), 8.92 (d, *J* = 4.8, 2H), 8.84 (s, 4H), 8.50–8.46 (m, 6H), 8.35–8.31 (m, 6H), 8.23 (d, *J* = 1.7 Hz, 2H), 7.97 (d, *J* = 3.6 Hz, 1H), 7.87 (d, *J* = 8.64 Hz, 2H), 7.69–7.66 (m, 2H), 7.61 (d, *J* = 3.6 Hz, 1H), 4.14 (s, 6H), 4.11 (s, 3H), 1.55 (s, 18H) −2.67 (s, 2H); IR (Neat, cm^{-1}): 3319, 1722, 1608, 1550, 1481, 1363, 1274, 1263, 1180, 1110, 975, 918, 875, 800, 763, 750; λ_{abs}/nm (CH_2Cl_2): 421, 517, 554, 591, 650; HRMS-ESI calcd for $C_{68}H_{57}N_5O_6S$ ($[M+H]^+$): 1072.4108, found 1072.4142.

5,10,15-tris(4-methoxycarbonylphenyl)20-(3,6-di-tert-butyl-9-phenyl-9H-carbazole)porphyrin (1BC3E). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.04 (d, *J* = 4.8 Hz, 2H), 8.89 (d, *J* = 4.8, 2H), 8.84 (s, 4H),

8.48–8.46 (m, 6H), 8.42 (d, *J* = 8.2 Hz, 2H), 8.34–8.30 (m, 6H), 8.27 (d, *J* = 1.6 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.65–7.62 (m, 2H), 4.13 (s, 9H), 1.55 (s, 18H), −2.73 (s, 2H); IR (Neat, cm^{-1}): 3314, 1721, 1609, 1517, 1467, 1370, 1271, 1103, 1056, 1029, 1019, 799, 762, 731; λ_{abs}/nm (CH_2Cl_2): 420, 516, 551, 591, 648; HRMS-ESI calcd for $C_{70}H_{59}N_5O_6$ ($[M+H]^+$): 1066.4544, found 1066.4584.

5,10,15-tris(4-methoxycarbonylphenyl)20-(2,5-di-O-dodecyl phenyl) porphyrin (1OD3E). mp > 300 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.86 (d, *J* = 5.2 Hz, 2H), 8.81 (s, 4H), 8.75(d, *J* = 4.1 Hz,2H), 8.47–8.44 (m, 6H), 8.33–8.30 (m, 6H), 7.69 (t, *J* = 8.4Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 2H) 4.12 (s, 9H), 3.84 (t, *J* = 6.4 Hz,4H) 1.19–1.15 (m, 4H), 1.06–0.98 (m, 8H), 0.96–0.90 (m, 8H), 0.87–0.80 (m, 10H) 0.71–0.64 (m, 4H), 0.59–0.51 (m, 4H), 0.39–0.31 (m, 8H) −2.69 (s, 2H); IR (Neat, cm^{-1}): 3307, 1718, 1604, 1433, 1269, 1142, 1174, 1099, 1018, 9664, 796, 734; λ_{abs}/nm (CH_2Cl_2): 420, 516, 551, 591, 640; HRMS-ESI calcd for $C_{74}H_{84}N_4O_8$ ($[M+H]^+$): 1157.6367, found 1157.6366.

5,10,15-tris(4-methoxycarbonylphenyl)20-(4-O-hexyl phenyl) porphyrin (1OH3E). mp > 300 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.92 (d, *J* = 4.8 Hz, 2H), 8.81–8.79 (m, 6H), 8.44 (d, *J* = 4.0 Hz, 6H), 8.31–8.29 (m, 6H) 8.10 (d, *J* = 8.4 Hz, 2H) 7.28 (*J* = 8.4 Hz, 2H), 4.25 (t, *J* = 6.4 Hz, 2H), 4.14 (s, 9H), 2.02–1.95 (m, 2H), 1.65–1.60 (m, 2H), 1.47–1.45 (m, 2H), 1.34–1.26 (m, 2H), 1.01–0.97 (m, 2 H),−2.77 (s, 2H); IR (Neat, cm^{-1}): 3307, 1718, 1604, 1433, 1269, 1142, 1174, 1099, 1018, 9664, 796, 734; λ_{abs}/nm (CH_2Cl_2): 420, 516, 551, 591, 650; HRMS-ESI calcd for $C_{56}H_{48}N_4O_7$ ($[M]^+$): 888.3523, found 888.3517.

5,10,15-tris(4-methoxycarbonylphenyl)20-(4-*N*,*N*-dipropylaniline) porphyrin (1NP3E). mp > 300 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.04 (d, *J* = 4.8 Hz, 2H), 8.78–8.75 (m, 6H), 8.45−8.24 (m, 6H) 8.31–8.28 (m, 6H) 8.03 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 4.13 (s, 6H), 4.11 (s, 3H), 3.50 (t, *J* = 7.6 Hz, 4H), 1.90–1.84 (m, 4H), 1.10–1.07 (m, 6H), −2.69 (s, 2H) ; IR (Neat, cm^{-1}): 3309, 1720, 1602, 1512, 1433, 1272, 1184, 1097, 1018, 960, 796, 734; λ_{abs}/nm (CH_2Cl_2): 415, 517, 571, 656; HRMS-ESI calcd for $C_{56}H_{49}N_5O_6$ ($[M]^+$): 887.3683, found 887.3677.

5,10,15-tris(4-methoxycarbonylphenyl)20-(4-*N*,*N*-dinonylaniline) porphyrin (1NN3E). 300 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.07 (d, *J* = 4.8 Hz, 2H), 8.80–8.79 (m, 6H), 8.47–8.46 (m, 6H), 8.33–8.30 (m, 6H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 4.13 (s, 6H), 4.12 (s, 3H), 3.52 (t, *J* = 7.6 Hz, 4H), 1.86 (m, 4H), 1.57–1.26 (m, 24H) 0.93–0.90 (m, 6H) −2.66 (s, 2H); IR (Neat, cm^{-1}): 3315, 1718, 1604, 1515, 1433, 1272, 1190, 1099, 1018, 962, 796, 736; λ_{abs}/nm (CH_2Cl_2): 415, 519, 572, 654; HRMS-ESI calcd for $C_{68}H_{73}N_5O_6$ ($[M]^+$): 1055.5561, found 1055.5555.

5,10,15-tris(4-methoxycarbonylphenyl)20-(4-hexyl-2-thienyl)porphyrinato zinc(II) (Zn_1TH_3E). mp > 300 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.27 (d, *J* = 4.7 Hz, 2H), 8.90 (d, *J* = 4.7 Hz, 2H), 8.88 (s, 2H), 8.41–8.38 (m, 6H), 8.29–8.27 (m, 6H), 7.70 (d, *J* = 3.3 Hz, 2H), 7.16 (d, *J* = 3.2 Hz, 2H), 4.07 (s, 6H), 3.12 (s, 3H), 3.12 (t, *J* = 7.6 Hz, 2H), 1.95 (*p*, *J* = 7.4 Hz, 2H), 1.59 (*p*, *J* = 7.2 Hz, 2H), 1.48–1.42 (m, 4 H), 0.96 (t, *J* = 6.3 Hz, 3H); IR (Neat, cm^{-1}): 1721, 1699, 1605, 1434, 1268, 1193, 1179, 1112, 1100, 997, 978; λ_{abs}/nm (CH_2Cl_2): 424, 552, 590 HRMS-MALDI-TOF calcd for $C_{54}H_{44}N_4O_6SZn$ ($[M+H]^+$): 941.2351, found 941.2350.

5,10,15-tris(4-methoxycarbonylphenyl)20-(3,6-di-tert-butyl-9-(thiophen-2-yl)-9H-carbazole)porphyrinato zinc(II) (Zn_1TC_3E). mp > 300 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.39 (d, *J* = 4.8 Hz, 2H), 8.97 (d, *J* = 4.8, 2H), 8.89 (s, 4H), 8.37–8.33 (m, 6H), 8.31–8.8.26 (m, 6H), 8.19 (d, *J* = 1.7 Hz, 2H), 7.96 (d, *J* = 3.5 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.62–7.59 (m, 2H), 7.59 (d, *J* = 3.6 Hz, 1H), 4.02 (s, 6H), 4.00 (s, 3H), 1.50 (s, 18H) ; IR (Neat, cm^{-1}): 1722, 1697, 1606, 1552, 1475, 1363, 1271, 1176, 1114, 1101, 1073, 995, 975, 910, 877, 808, 792, 761; λ_{abs}/nm (CH_2Cl_2): 424, 552, 595; HRMS-FAB calcd for $C_{68}H_{55}N_5O_6SZn$ ($[M+H]^+$): 1134.3243, found 1134.3274.

5,10,15-tris(4-methoxycarbonylphenyl)20-(3,6-di-tert-butyl-9-phenyl-9H-carbazole)porphyrinato zinc(II) (Zn_1BC_3E). mp > 300 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.13 (d, *J* = 4.6 Hz, 2H), 8.98 (d, *J* = 4.7, 2H), 8.92 (s, 4H), 8.42 (d, *J* = 8.1 Hz, 2H), 8.40–8.36 (m, 6H), 8.33–8.29 (m, 6H), 8.26 (d, *J* = 1.4 Hz, 2H), 7.98 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.62–7.60 (m, 2H), 4.04 (s, 6H), 4.04 (s, 3H), 1.54 (s, 18H); IR (Neat, cm^{-1}): 1721, 1698, 1609, 1462, 1265, 1105, 1056, 998, 809, 762, 757; λ_{abs}/nm (CH_2Cl_2): 422, 549, 587; HRMS-FAB calcd for $C_{70}H_{57}N_5O_6Zn$ ($[M+H]^+$): 1128.3679, found 1128.3723.

5,10,15-tris(4-methoxycarbonylphenyl)20-(2,5-di-O-dodecyl phenyl) porphyrinato zinc (II) (Zn_1OD_3E). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.93 (d, *J* = 4.8 Hz, 2H), 8.88 (s, 4H), 8.82(d, *J* = 4.4 Hz, 2H), 8.41–8.39 (m, 6H), 8.31–8.27 (m, 6H), 7.68 t (*J* = 8.4 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 4.08 (s, 6H), 4.07 (s, 3H), 3.83 (t, *J* = 6.4 Hz, 4H), 1.18–1.12 (m, 4H), 1.04–0.98 (m, 4H), 0.94–0.93 (m, 8H), 0.81–0.74 (m, 6H) 0.73–0.69 (m, 4H), 0.60–0.53 (m, 4H), 0.47–0.36 (m, 8H) 0.29–0.21 (m, 8H) ; IR (Neat, cm^{-1}): 1787, 1602, 1515, 1403, 1263, 1193, 990, 785, 762; λ_{abs}/nm (CH_2Cl_2): 422, 550, 592; HRMS-ESI calcd for $C_{74}H_{82}N_4O_8Zn$ ($[M]^+$): 1218.5424, found 1218.5424.

5,10,15-tris(4-methoxycarbonylphenyl)20-(4-O-hexyl phenyl) porphyrinato zinc (II) (Zn_1OH_3E). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.02 (d, *J* = 4.8 Hz, 2H), 8.89–8.88 (m, 6H), 8.40 (d, *J* = 8.0 Hz, 6H), 8.30–8.28 (m, 6H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 4.8 Hz, 2H), 4.24 (t, *J* = 6.8 Hz, 2H), 4.07 (s, 9H), 2.01–1.94 (m, 2H), 1.67–1.59 (m, 4H), 1.00–0.97 (m, 3H), IR (Neat, cm^{-1}): 1722, 1604, 1433, 1271, 1176, 1099, 995, 819, 761, 713; λ_{abs}/nm (CH_2Cl_2): 422, 548, 588; HRMS-ESI calcd for $C_{56}H_{46}N_4O_7Zn$ ($[M]^+$): 950.2658, found 950.2652.

5,10,15-tris(4-methoxycarbonylphenyl)20-(4-*N*,*N*-dipropylaniline) porphyrinato zinc (II) (Zn_1NP_3E). 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.14 (d, *J* = 4.8 Hz, 2H), 8.78–8.86 (m, 6H), 8.55–8.23 (m, 6H) 8.41–8.318 (m, 6H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 4.23 (s, 6H), 4.21 (s, 3H), 3.60 (t, *J* = 7.6 Hz, 2H), 1.94 (m, 4H), 1.20–1.17 (m, 6H) ; IR (Neat, cm^{-1}): 1710, 1600, 1433, 1269, 1182, 1101, 995, 815, 761, 713; λ_{abs}/nm (CH_2Cl_2): 418, 552, 601; HRMS-ESI calcd for $C_{56}H_{47}N_5O_6Zn$ ($[M]^+$): 949.2818, found 949.2812.

5,10,15-tris(4-methoxycarbonylphenyl)20-(4-*N*,*N*-dinonylaniline) porphyrinato zinc (II) (Zn_1NN_3E). 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.15 (d, *J* = 4.8 Hz, 2H), 8.87–8.86 (m, 6H), 8.37–8.35 (m, 6H), 8.30–8.28 (m, 6H), 8.02 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 4.03 (s, 6H), 4.02 (s, 3H), 3.51 (t, *J* = 7.2 Hz, 4H), 1.82 (m, 4H), 1.45–1.40 (m, 8H), 1.38–1.31 (m, 16H), 0.97–0.87 (m, 6H); IR (Neat, cm^{-1}): 1722, 1604, 1434, 1272, 1190, 1107, 995, 819, 792, 763; λ_{abs}/nm (CH_2Cl_2): 417, 553, 600; HRMS-ESI calcd for $C_{68}H_{71}N_5O_6Zn$ ($[M]^+$): 1117.4696, found 1117.4690.

5,10,15-tris(4-carboxylphenyl)20-(4-hexyl-2-thienyl)porphyrinato zinc(II) (Zn_1TH_3A). mp > 300 °C; ^{1}H NMR (400 MHz, DMSO-D_6) δ = 13.22 (s, 3H), 9.05 (d, *J* = 4.6 Hz, 2H), 8.76–8.26 (m 6H), 8.36–8.33 (m, 6H), 8.28–8.26 (m, 6H), 7.70 (d, *J* = 3.2 Hz, 2H), 7.25 (d, *J* = 3.2 Hz, 2H), 3.09 (t, *J* = 7.5 Hz, 2H), 1.89 (*p*, *J* = 7.5 Hz, 2H), 1.55 (*p*, *J* = 7.3 Hz, 2H), 1.59–1.51 (m, 4 H), 0.93 (t, *J* = 6.9 Hz, 3H); IR (Neat, cm^{-1}): 3352, 1683, 1602, 1408, 1337, 1313, 1268, 1204, 1071, 997, 872; λ_{abs}/nm (THF), ($\varepsilon/10^3$ $M^{-1}\cdot cm^{-1}$): 427 (350), 558 (18), 600 (9); λ_{em}/nm (THF): 612, 656; HRMS-FAB calcd for $C_{51}H_{38}N_4O_6SZn$ ($[M^+]$): 898.1804, found 898.1802, EA calcd for $C_{51}H_{38}N_4O_6SZn$: C 68.04%, H 4.25%, N 6.22%; found C 68.12%, H 4.29%, N 6.11%.

5,10,15-tris(4-carbonylphenyl)20-(3,6-di-tert-butyl-9-(thiophen-2-yl)-9H-carbazole)porphyrinato zinc(II) (Zn_1TC_3A). mp > 300 °C; ^{1}H NMR (400 MHz, DMSO-D_6) δ = 13.25 (s, 3H), 9.30 (d, *J* = 4.7 Hz, 2H), 8.87 (d, *J* = 4.7, 2H), 8.79 (s, 4H), 8.38–8.36 (m, 6H), 8.40 (s, 2H), 8.34–8.30 (m, 6H), 8.07 (d, *J* = 3.5 Hz, 1H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.81 (d, *J* = 3.6 Hz, 1H), 7.68–7.65 (m, 1H), 1.47 (s, 18H); IR (Neat, cm^{-1}): 1722, 1606, 1550, 1485, 1363, 1276, 1263, 1178, 1110, 1020, 975, 948, 800, 750; λ_{abs}/nm (THF), ($\varepsilon/10^3$ $M^{-1}\cdot cm^{-1}$): 426 (409), 558 (17), 599 (6); λ_{em}/nm (THF): 605, 654; HRMS-FAB calcd for $C_{65}H_{49}N_5O_6SZn$ ($[M+H]^+$): 1092.2773, found 1092.2803, EA calcd for $C_{65}H_{49}N_5O_6SZn$: C 71.39%, H 4.52%, N 6.40%; found C 71.47%, H 4.45%, N 6.11%.

5,10,15-tris(4-carbonylphenyl)20-(3,6-di-tert-butyl-9-phenyl-9H-carbazole)porphyrinato zinc(II) (Zn_1BC_3A). mp > 300 °C; ^{1}H NMR (400 MHz, DMSO-D_6) δ = 13.46 (s, 3H), 9.03 (d, *J* = 4.5 Hz, 2H), 8.87 (d, *J* = 4.6, 2H), 8.82 (s, 4H), 8.44 (d, *J* = 8.1 Hz, 2H), 8.41 (m, 2H), 8.40–8.37 (m, 6H), 8.34–8.30 (m, 6H), 8.26 (d, *J* = 1.4 Hz, 2H), 8.04 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.6 Hz, 2H), 7.65–7.62 (m, 2H), 1.54 (s, 18H); IR (Neat, cm^{-1}): 1687, 1604, 1509, 1481, 1362, 1271, 126, 1053, 1037, 995, 799, 759, 749; λ_{abs}/nm (THF), ($\varepsilon/10^3$ M^{-1} cm^{-1}): 426 (452), 557 (19), 598 (7); λ_{em}/nm (THF): 606, 658; HRMS-FAB calcd for $C_{67}H_{51}N_5O_6Zn$ ($[M+H]^+$): 1086.3209, found 1086.3260, EA calcd for $C_{67}H_{51}N_5O_6Zn$: C 74.00%, H 4.73%, N 6.44%; found C 68.12%, H 4.29%, N 6.11%.

5,10,15-tris(4-carbonylphenyl)20-(2,5-di-O-dodecyl phenyl) porphyrinato zinc (II) (Zn_1OD_3A). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-D_6) δ = 13.24 (s, 3H) 8.75 (s, 4H), 8.71 (d, *J* = 4.8 Hz, 2H), 8.67 (d, *J* = 4.4 Hz, 2H), 8.36–8.34 (m, 6H), 8.27–8.24 (m, 6H) 7.64 (t, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.80 (t, *J* = 6.4 Hz, 4H) 1.18–1.12 (m, 8H), 1.06–0.97 (m, 8H), 0.98–0.76 (m, 10 H), 0.70–0.66 (m, 4H) 0.59–0.56 (m, 4H), 0.36–0.32 (m, 4H), 0.22–0.19 (m, 4H) ; IR (Neat, cm^{-1}): 1789, 1604, 1454, 1417, 1272, 1095, 995, 794, 763, 717; λ_{abs}/nm (THF), (ε/10^3 $M^{-1}\cdot cm^{-1}$): 426 (391), 557 (18), 597 (7); λ_{em}/nm (THF): 605, 657; HRMS-ESI calcd for $C_{71}H_{76}N_4O_8Zn$ ($[M]^+$): 1176.4955, found 1176.4955, EA calcd for $C_{71}H_{76}N_4O_8Zn$: C 72.34%, H 6.50%, N 4.75%; found C 72.23%, H 6.57%, N 4.71%.

5,10,15-tris(4-carbonylphenyl)20-(4-O-hexyl phenyl) porphyrinato zinc (II) (Zn_1OH_3A). 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-D_6) δ = 12.90 (s, 3H), 8.85 (d, *J* = 4.8 Hz, 2H), 8.77–8.75 (m, 6H), 8.34 (d, *J* = 8.0 Hz, 6H), 8.24 (d, *J* = 8.0 Hz, 6H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.20 (t, *J* = 6.4 Hz, 2H), 1.44–1.40 (m, 2H), 1.59–1.54 (m, 2H), 1.44–1.40 (m, 4H), 0.96–0.92 (m, 3H); IR (Neat, cm^{-1}): 1691, 1602, 1506, 1400, 1271, 1174, 1099, 991, 790, 765; λ_{abs}/nm (THF), (ε/10^3 $M^{-1}\cdot cm^{-1}$): 426(471), 557(18), 597(7); λ_{em}/nm (THF): 607, 656; HRMS-ESI calcd for $C_{53}H_{40}N_4O_7Zn$ ($[M]^+$): 908.2188, found 908.2182, EA calcd for $C_{53}H_{40}N_4O_7Zn$: C 69.93%, H 4.43%, N 6.15%; found C 70.12%, H 4.39%, N 5.98%.

5,10,15-tris(4-carbonylphenyl)20-(4-*N*,*N*-dipropylaniline) porphyrinato zinc (II) (Zn_1NP_3A). 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-D_6) δ = 12.93 (s, 3H), 8.96 (d, *J* = 4.4 Hz, 2H), 8.76–8.74 (m, 6H), 8.36–8.233(m, 6H), 8.26–8.24 (m, 6H), 7.94 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.48 (t, *J* = 6.4 Hz, 4H), 1.84–1.78 (m, 4H), 1.06–1.03 (m, 6H); IR (Neat, cm^{-1}): 1682, 1600, 1515, 1415, 1272, 1195, 1091, 993, 794, 763, 750; λ_{abs}/nm (THF), (ε/10^3 $M^{-1}\cdot cm^{-1}$): 426 (248), 560 (18), 604 (11); λ_{em}/nm (THF): 621; HRMS-ESI calcd for $C_{53}H_{41}N_5O_6Zn$ ($[M]^+$): 907.2348, found 907.2342, EA calcd for $C_{53}H_{41}N_5O_6Zn$: C 70.01%, H 4.54%, N 7.70%; found C 69.91%, H 4.60%, N 7.79%.

5,10,15-tris(4-carbonylphenyl)20-(4-*N*,*N*-dinonylaniline) porphyrinato zinc (II) (Zn_1NN_3A). 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-D_6) δ = 12.66 (s, 3H), 8.96 (m, 2H), 8.75 (m, 6H), 8.34–8.32 (m, 6H), 8.21 (m, 6H), 7.93–7.92 (m, 2H), 6.94–6.85 (m, 2H), 3.47 (m, 4H), 1.76 (m, 4H), 1.40–1.14 (m, 24H); I0.83–0.82 (m 6H); IR (Neat, cm^{-1}): 1684, 1604, 1434, 1270, 1188, 1110, 997, 821, 795, 769; λ_{abs}/nm (THF), (ε/10^3 $M^{-1}\cdot cm^{-1}$): 425 (143), 560 (12), 603 (8); λ_{em}/nm (THF): 624; HRMS-ESI calcd for $C_{65}H_{65}N_5O_6Zn$ ($[M]^+$): 1075.4226, found 1075.4220, EA calcd for $C_{65}H_{65}N_5O_6Zn$: C 72.45%, H 6.08%, N 6.50%; found C 72.41%, H 7.94%, N 6.51%.

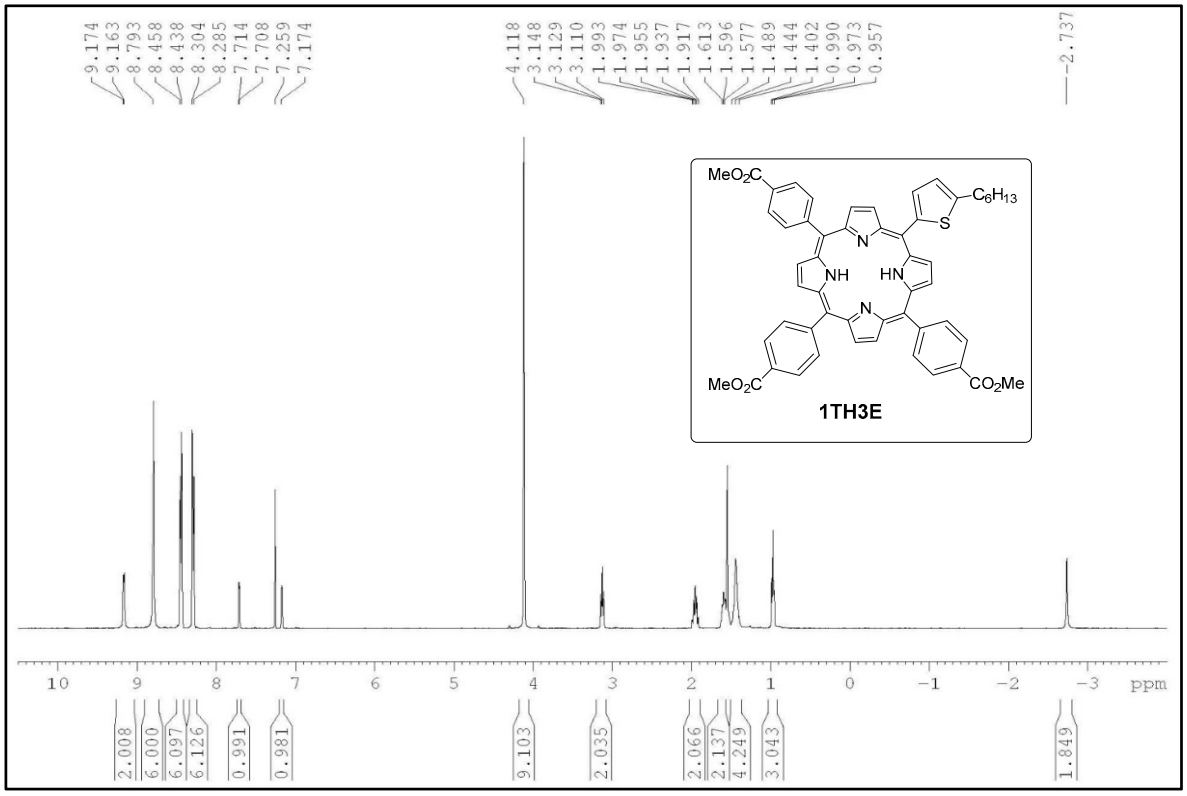


Figure S2. Nuclear magnetic resonance (NMR) and spectrum of 1TH3E.

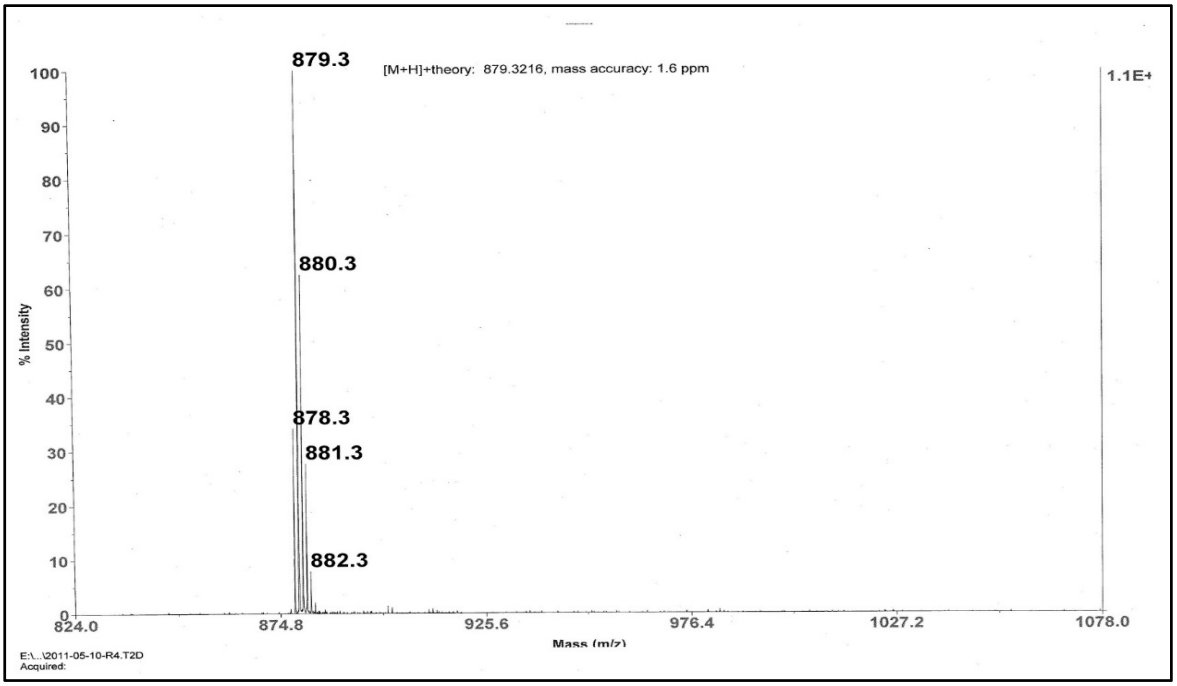


Figure S3. High resolution mass spectrometer (HRMS) of 1TH3E.

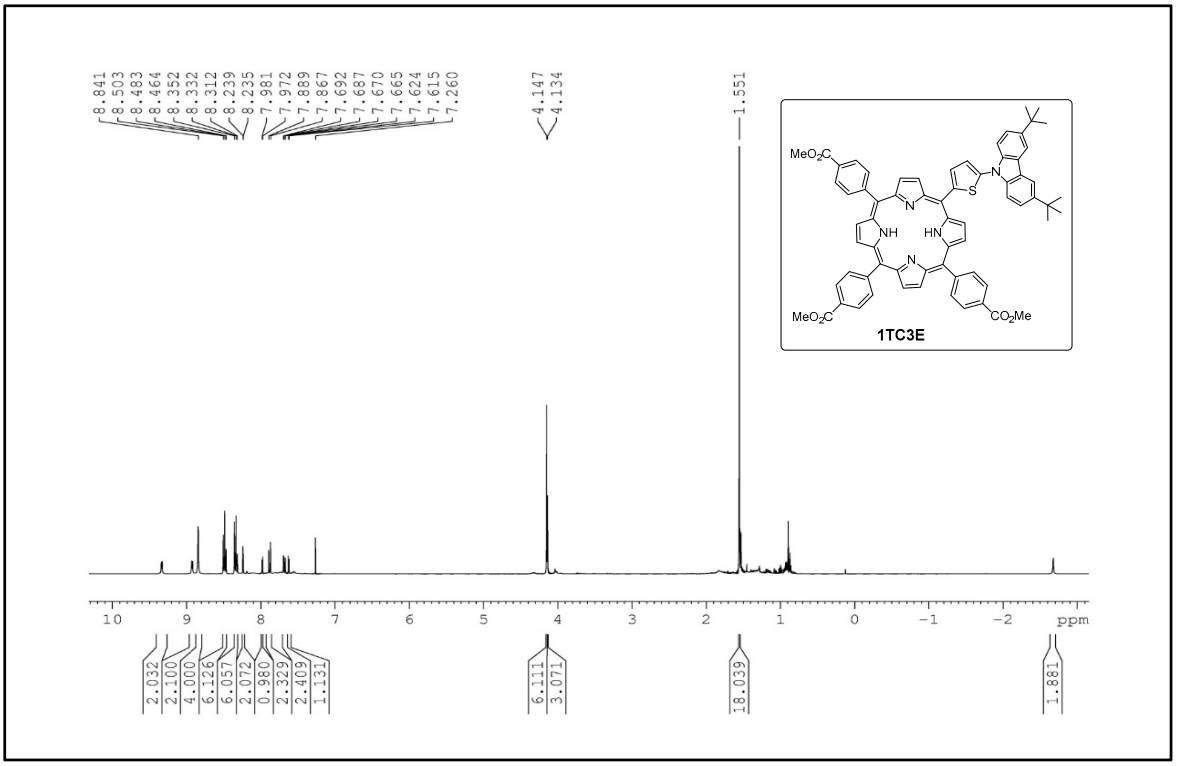


Figure S4. NMR spectrum of 1TC3E.

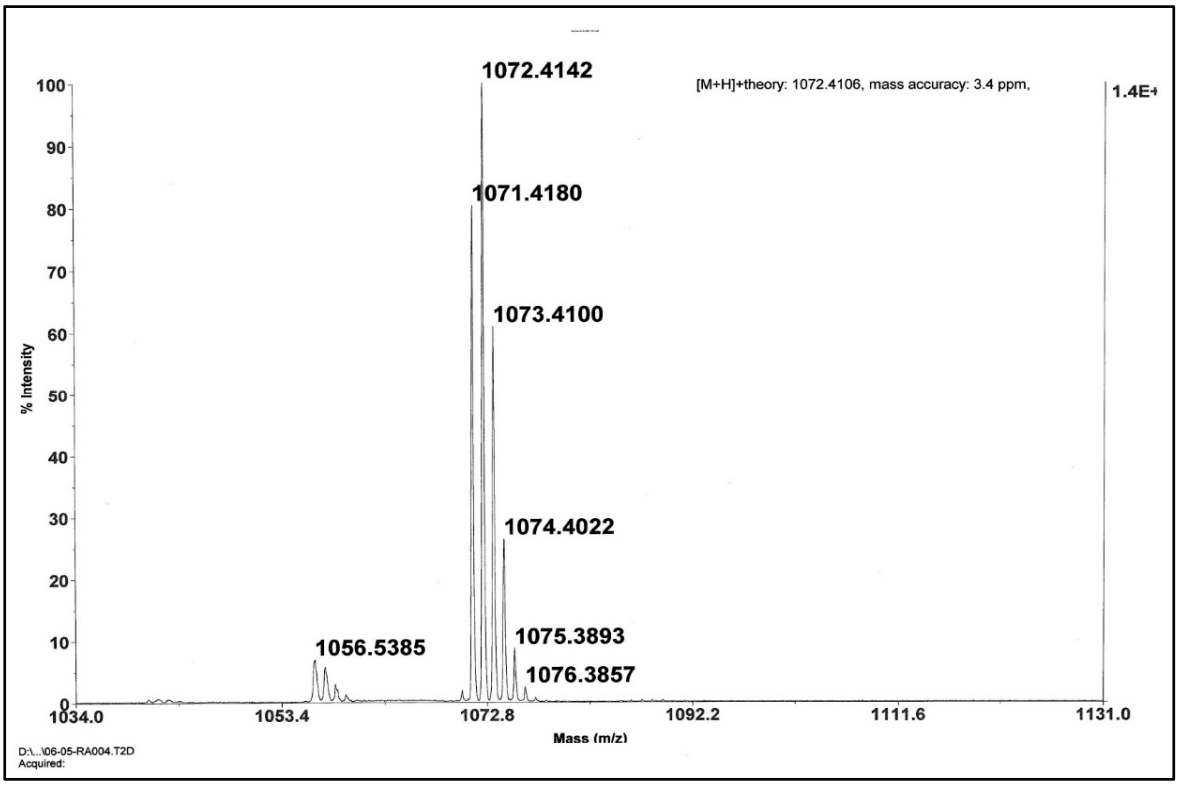


Figure S5. HRMS of 1TC3E.

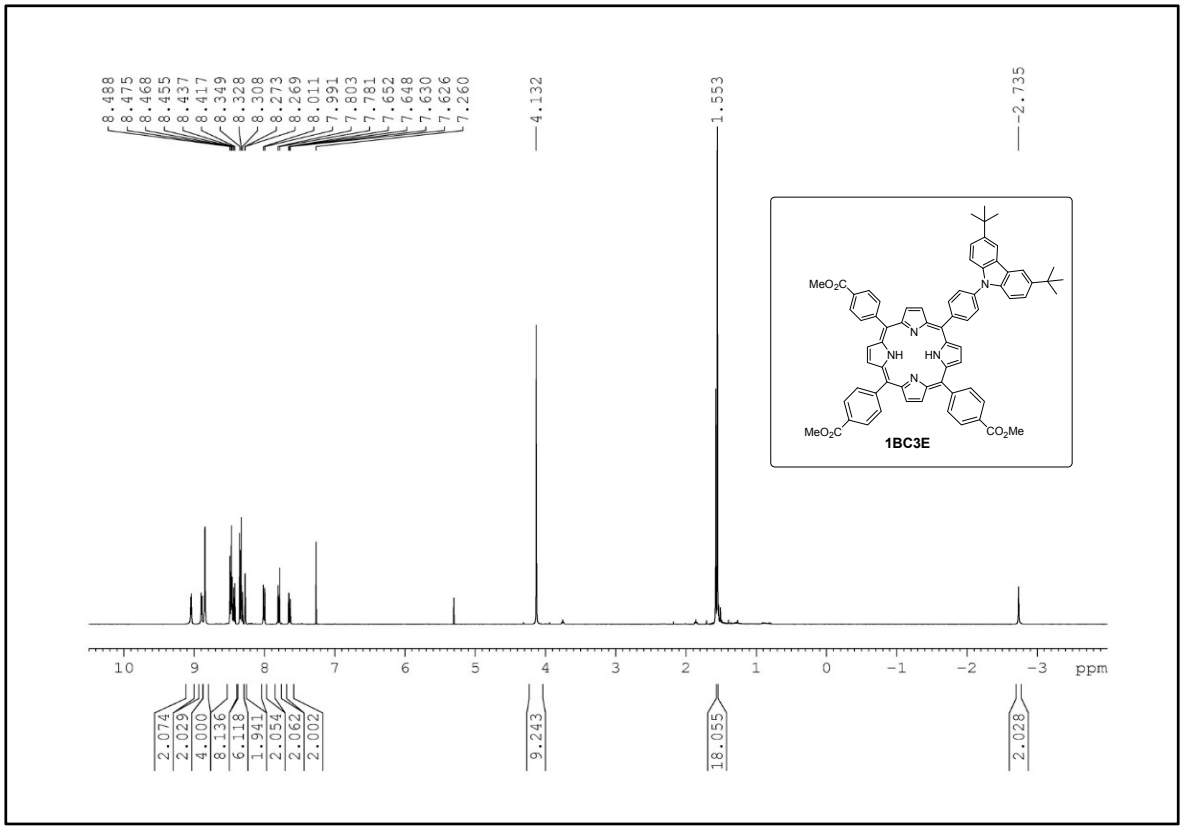


Figure S6. NMR spectrum of 1BC3E.

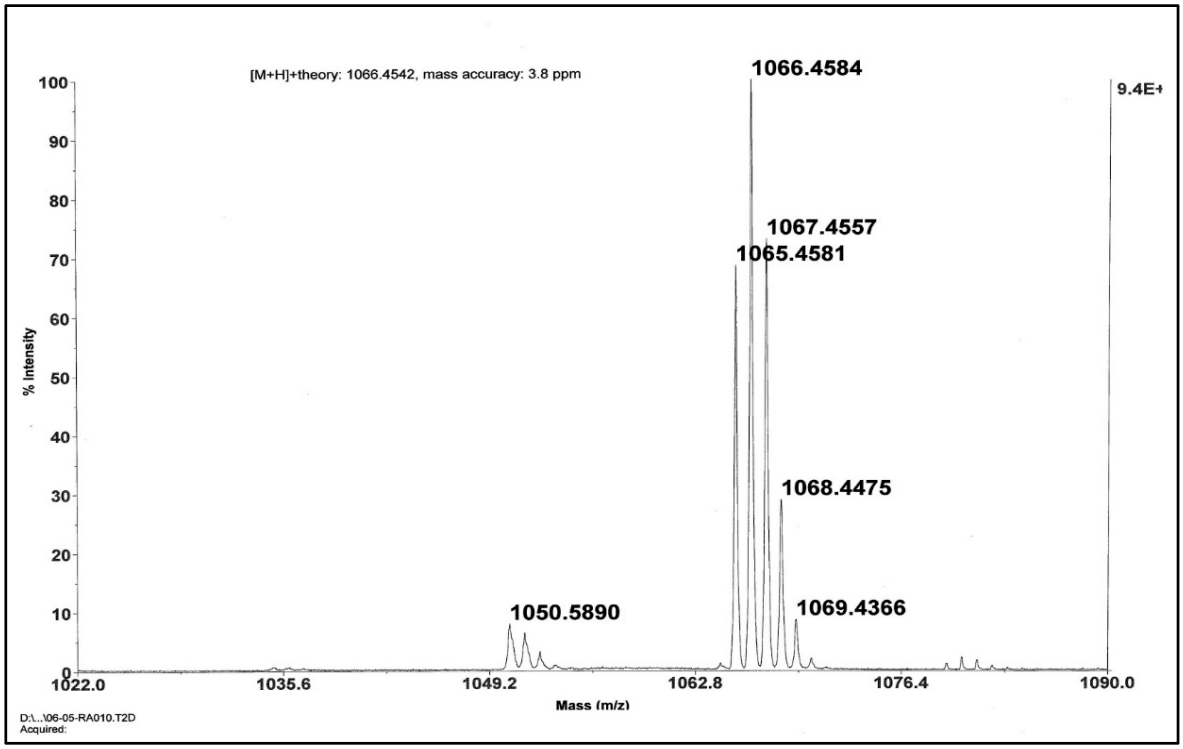


Figure S7. HRMS of 1BC3E.

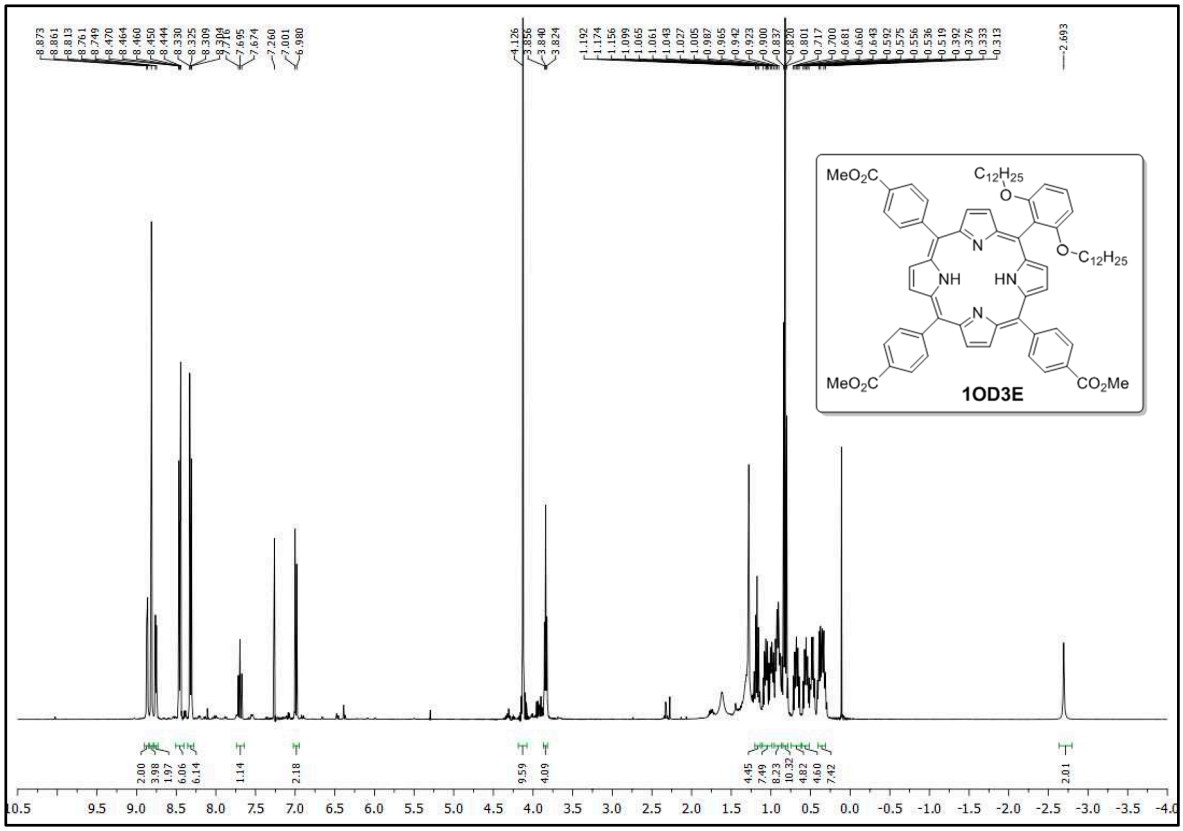


Figure S8. NMR spectrum of 1OD3E.

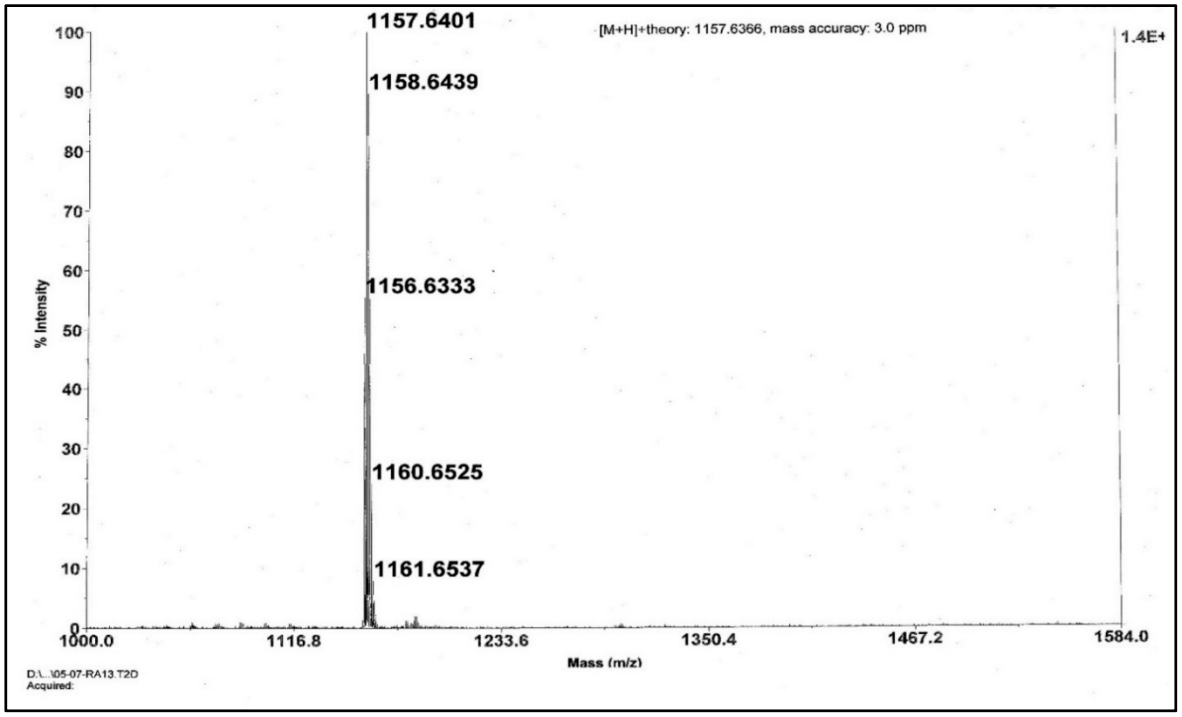


Figure S9. HR-MS of 1OD3E.

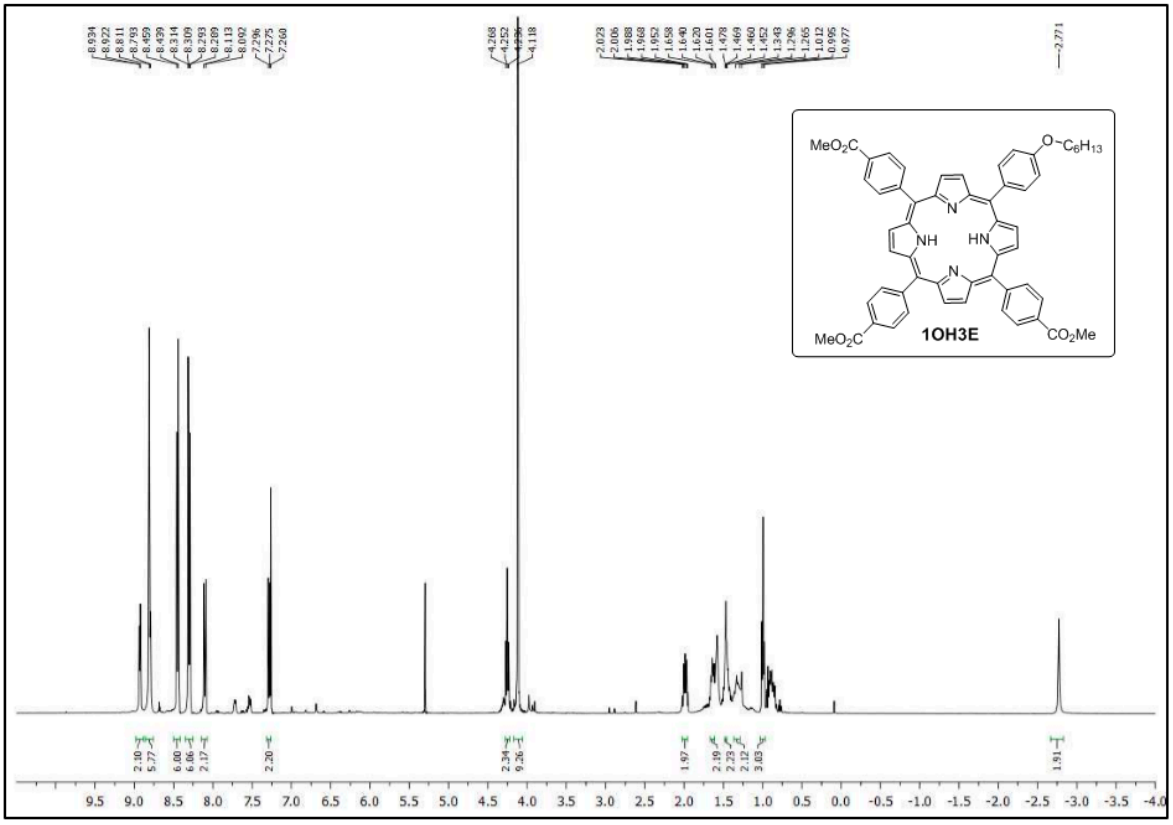


Figure S10. NMR spectrum of 1OH3E.

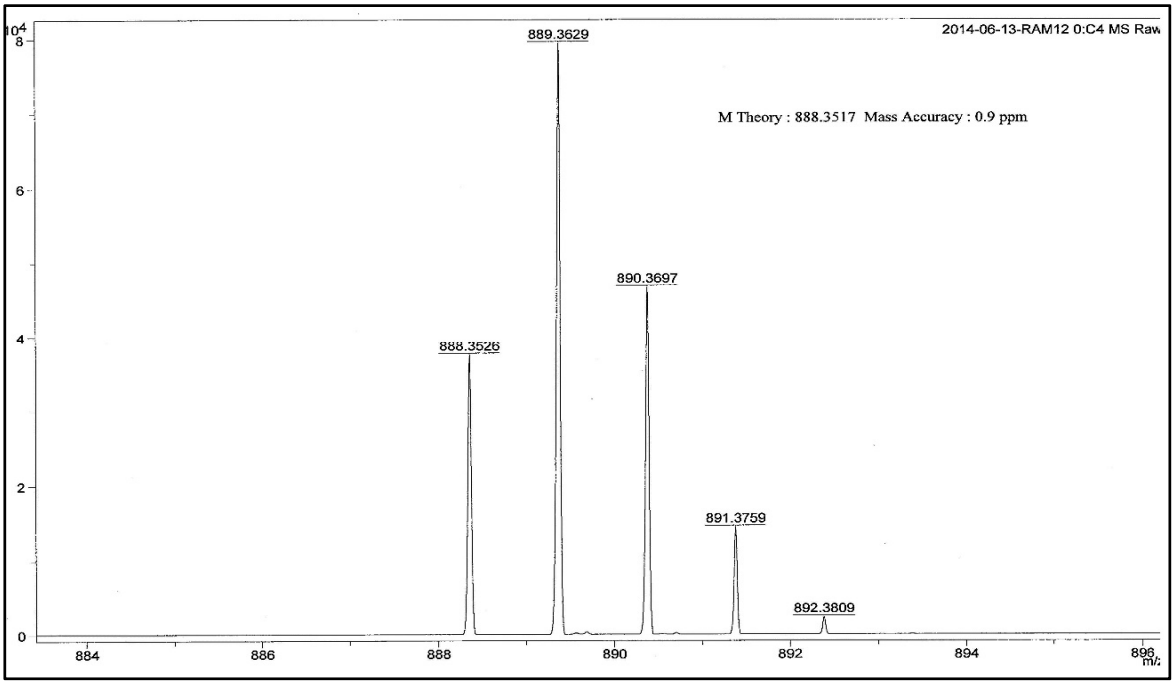


Figure S11. HR-MS of 1OH3E.

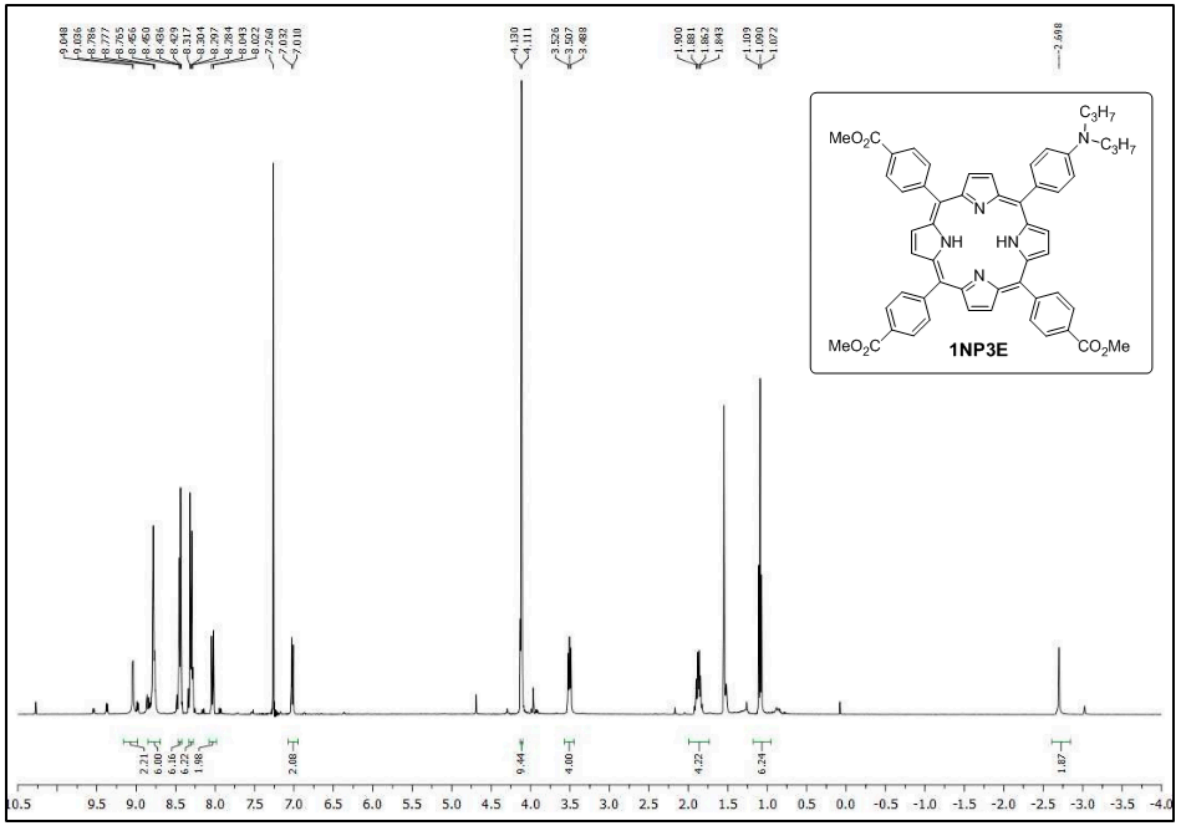


Figure S12. NMR spectrum of 1NP3E.

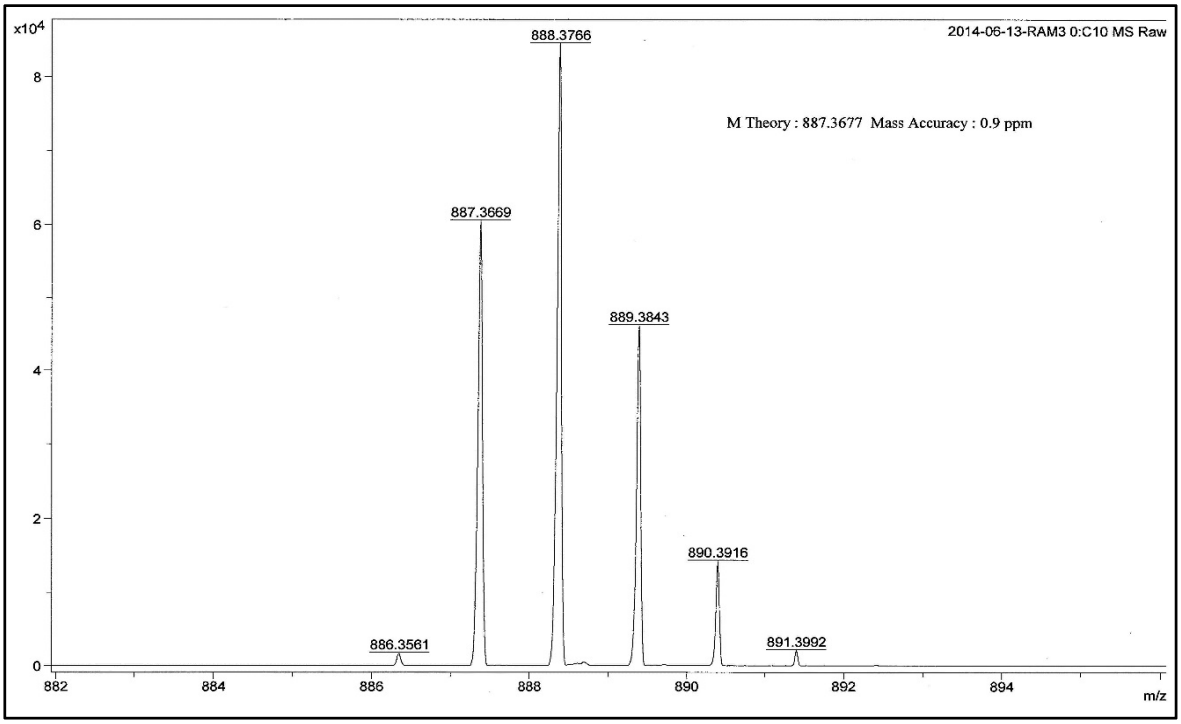


Figure S13. HRMS of 1NP3E.

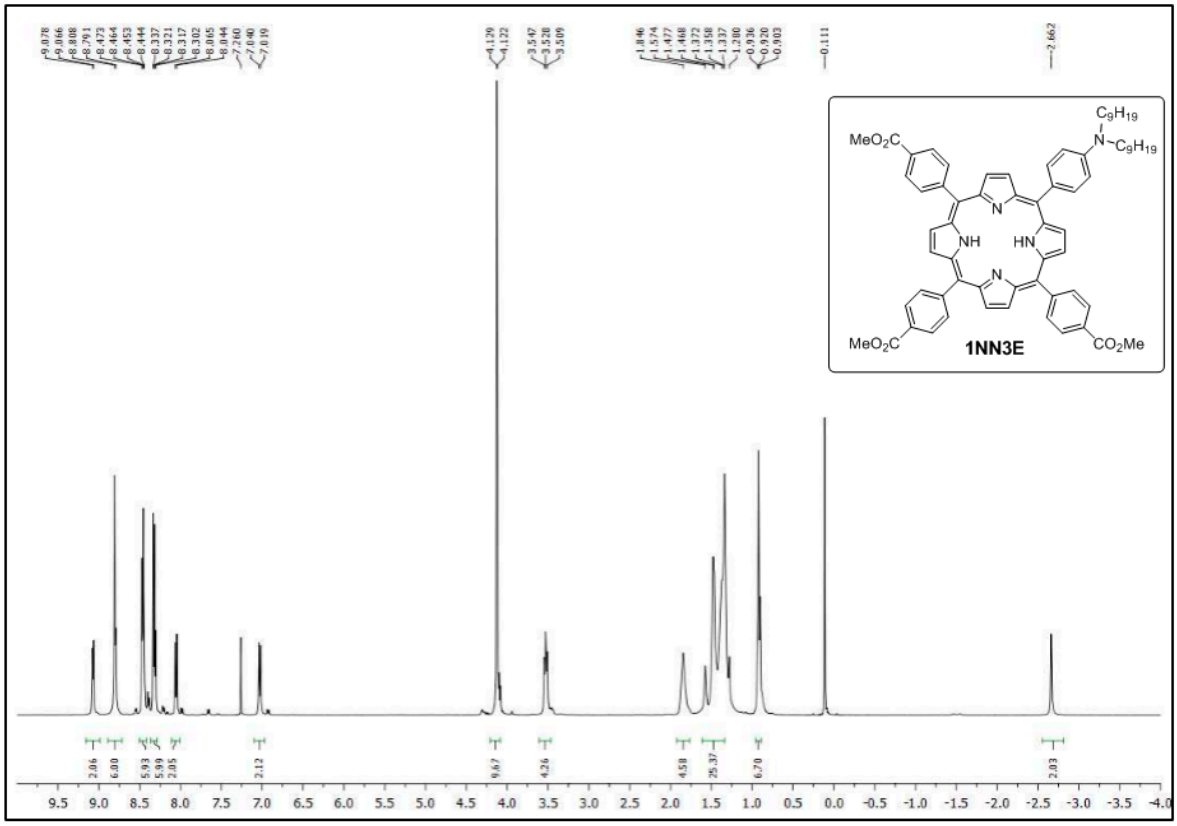


Figure S14. NMR spectrum of 1NN3E.

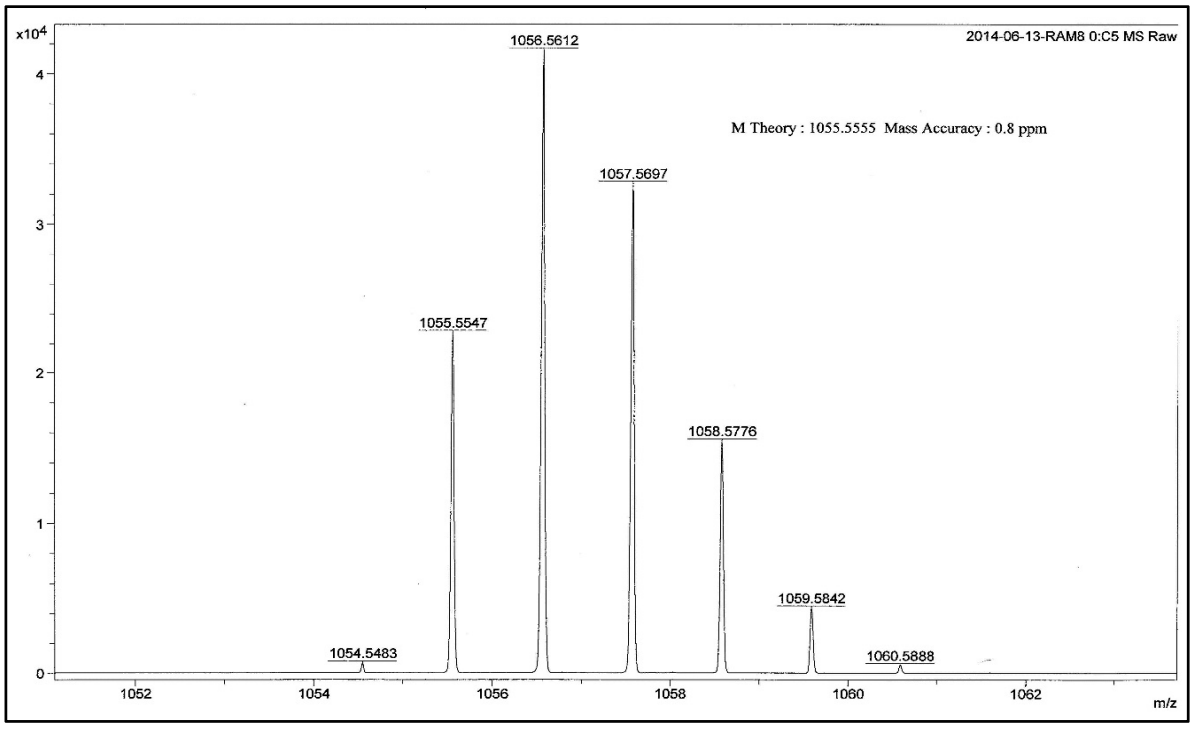


Figure S15. HRMS of 1NN3E.

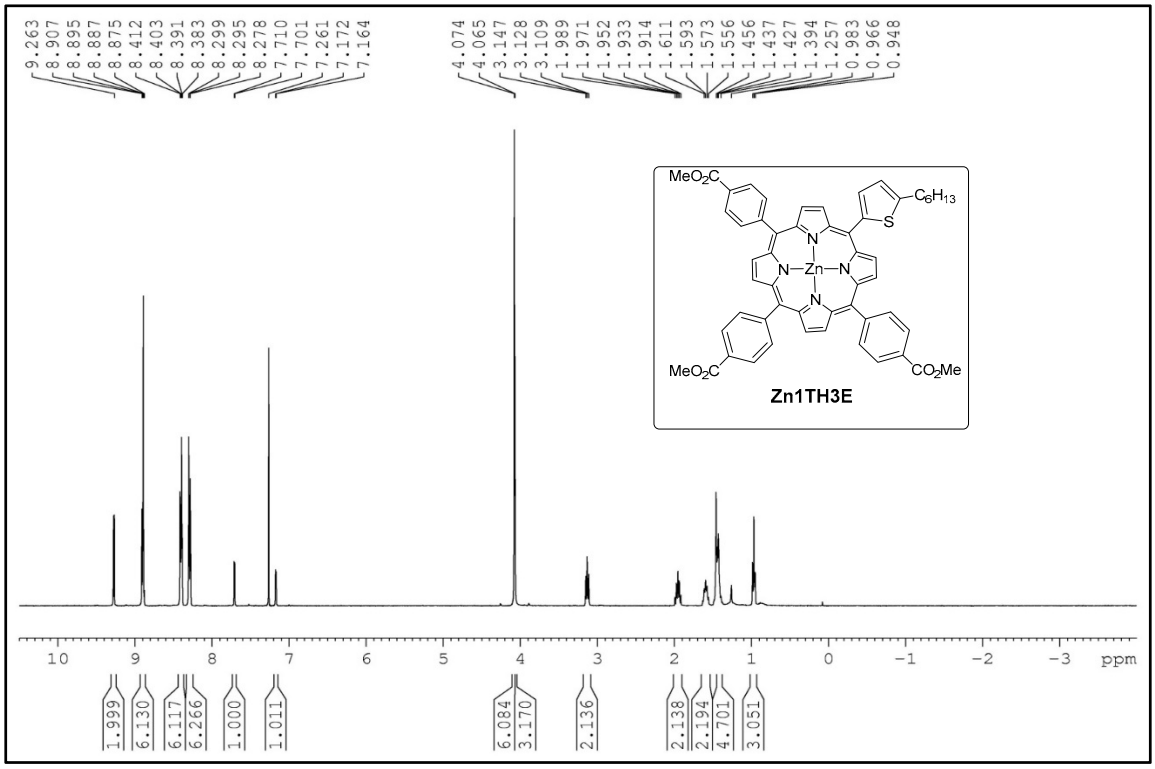


Figure S16. NMR spectrum of Zn_1TH_3E.

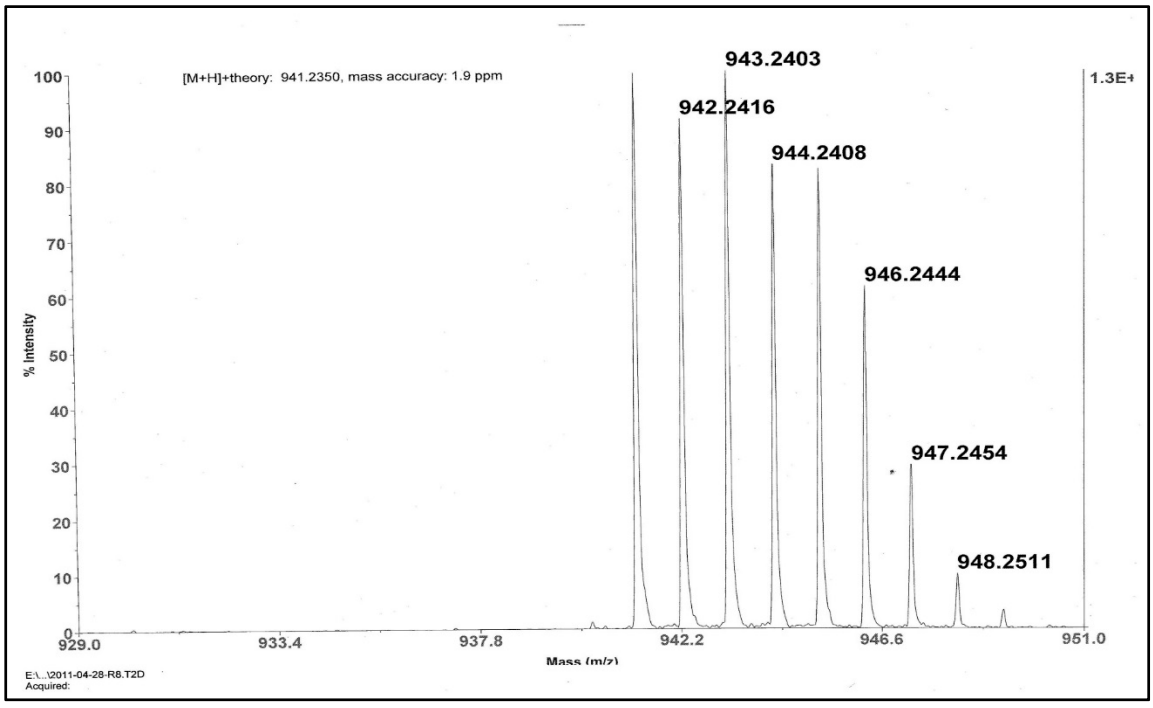


Figure S17. HRMS of Zn_1TH_3E.

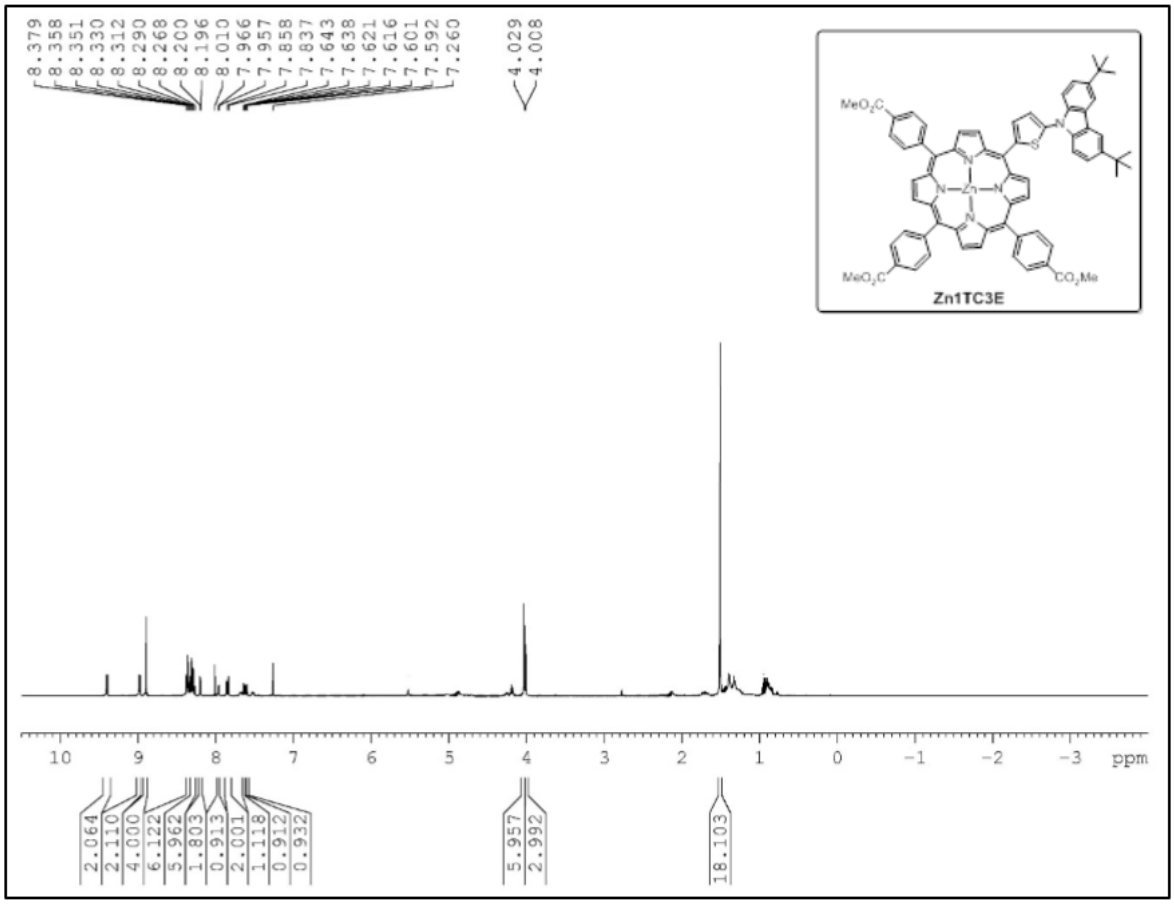


Figure S18. NMR spectrum of Zn_1TC_3E.

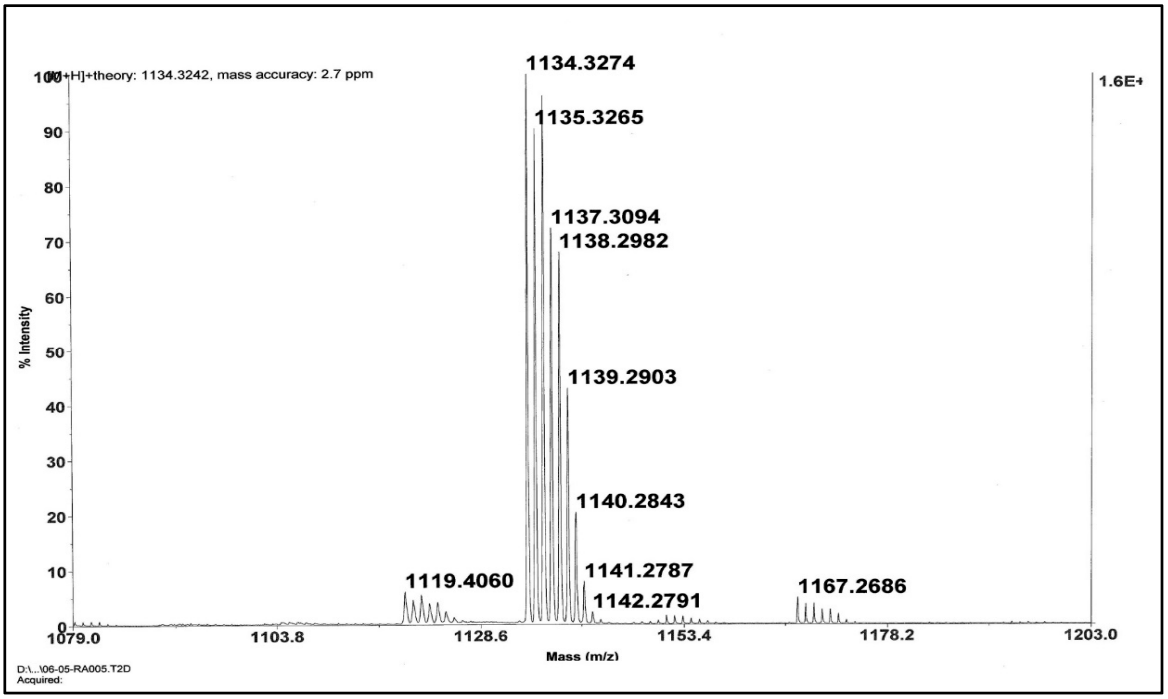


Figure S19. HRMS of Zn_1TC_3E.

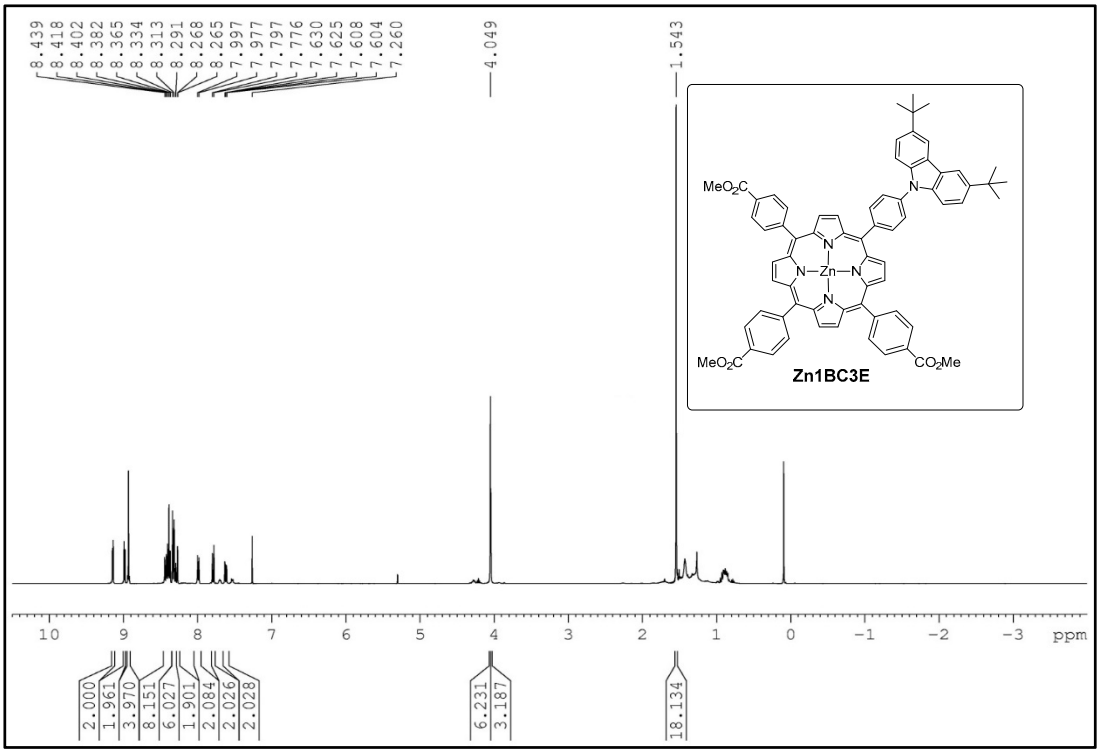


Figure S20. NMR spectrum of Zn1BC3E.

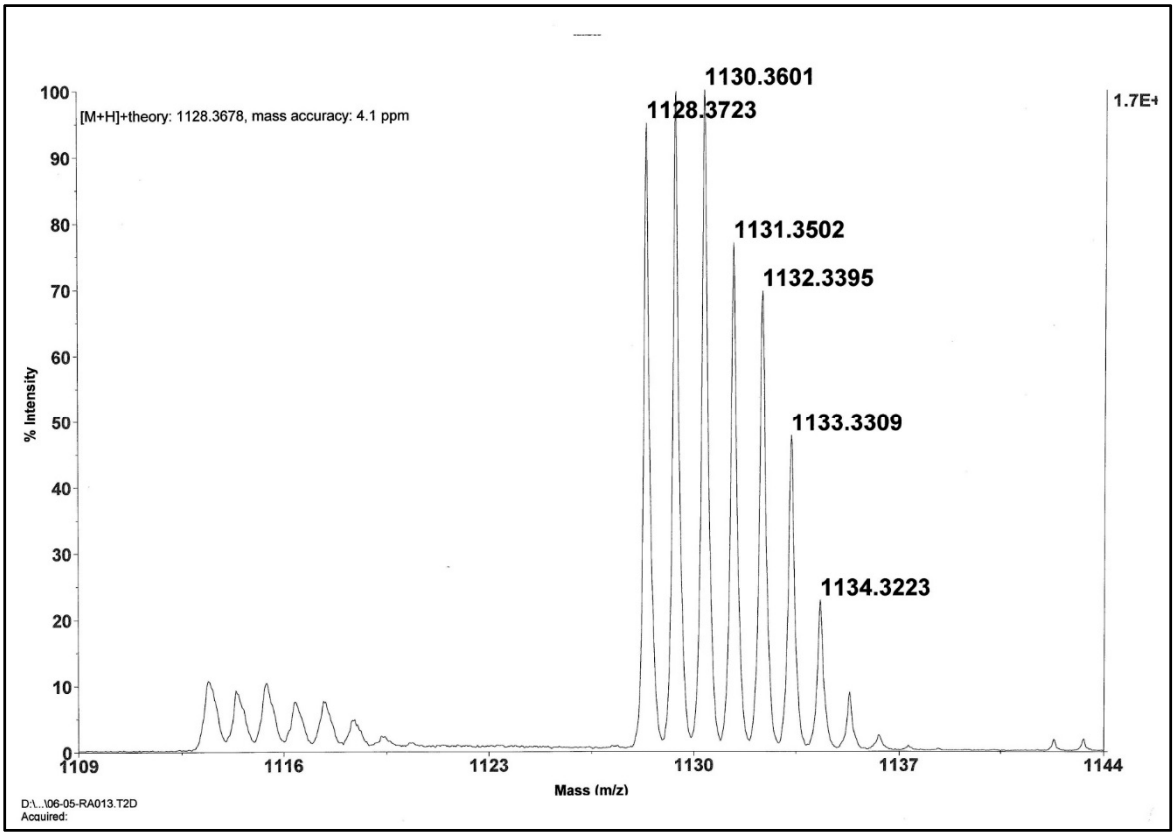


Figure S21. HRMS of Zn1BC3E.

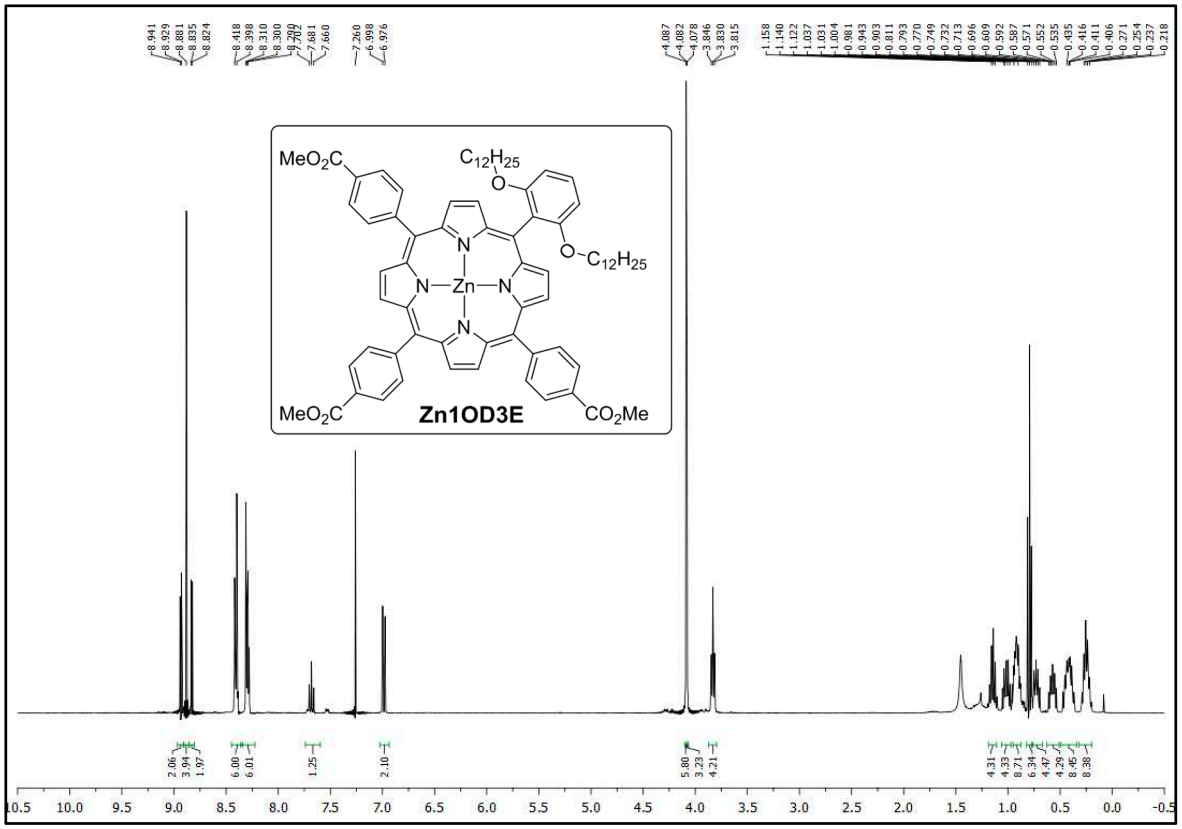


Figure S22. NMR spectrum of Zn_1OD_3E.

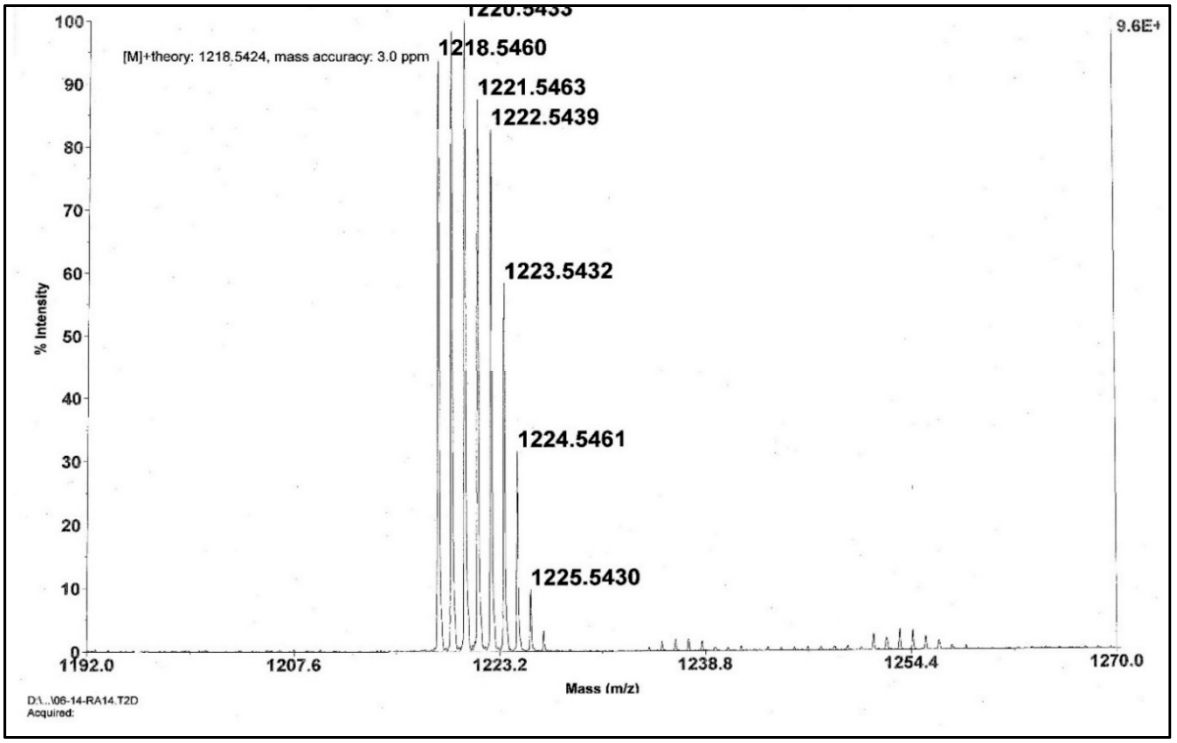


Figure S23. HRMS of Zn_1OD_3E.

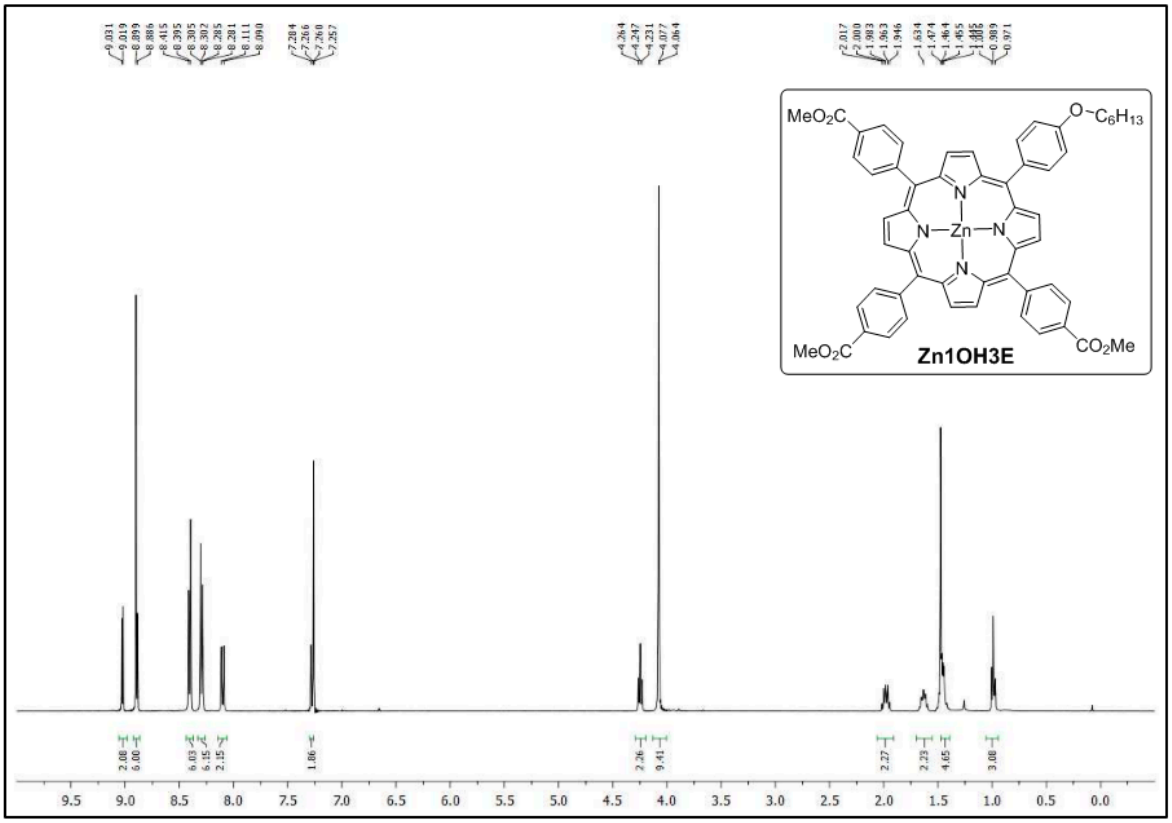


Figure S24. NMR spectrum of Zn_1OH_3E.

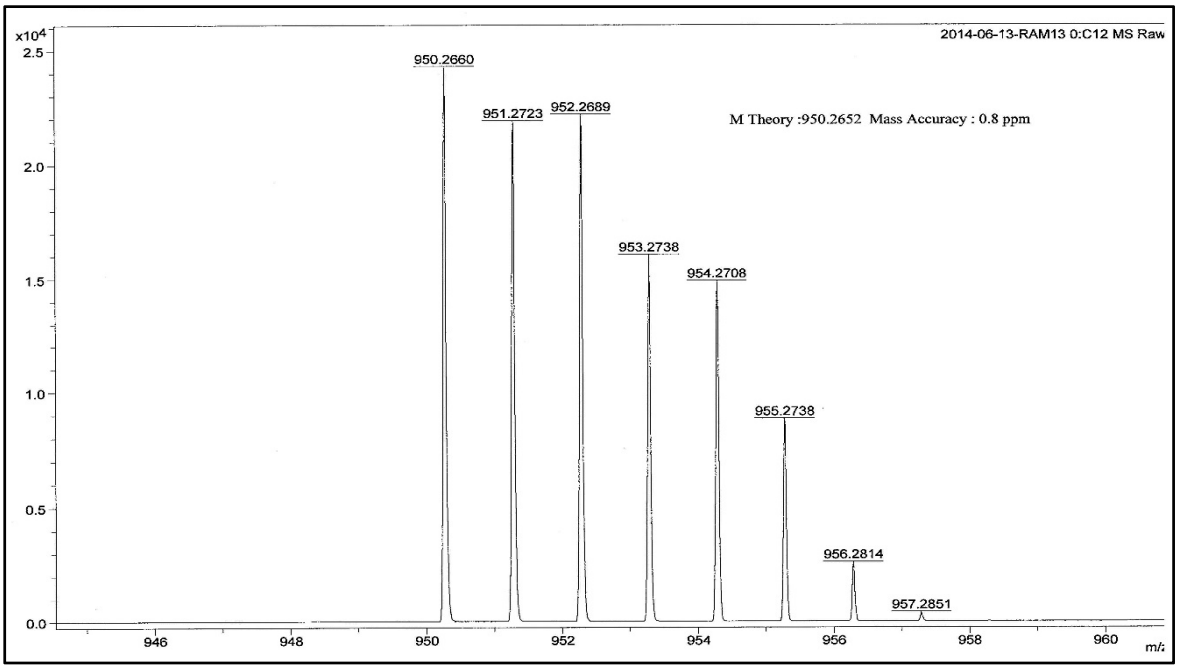


Figure S25. HRMS of Zn_1OH_3E.

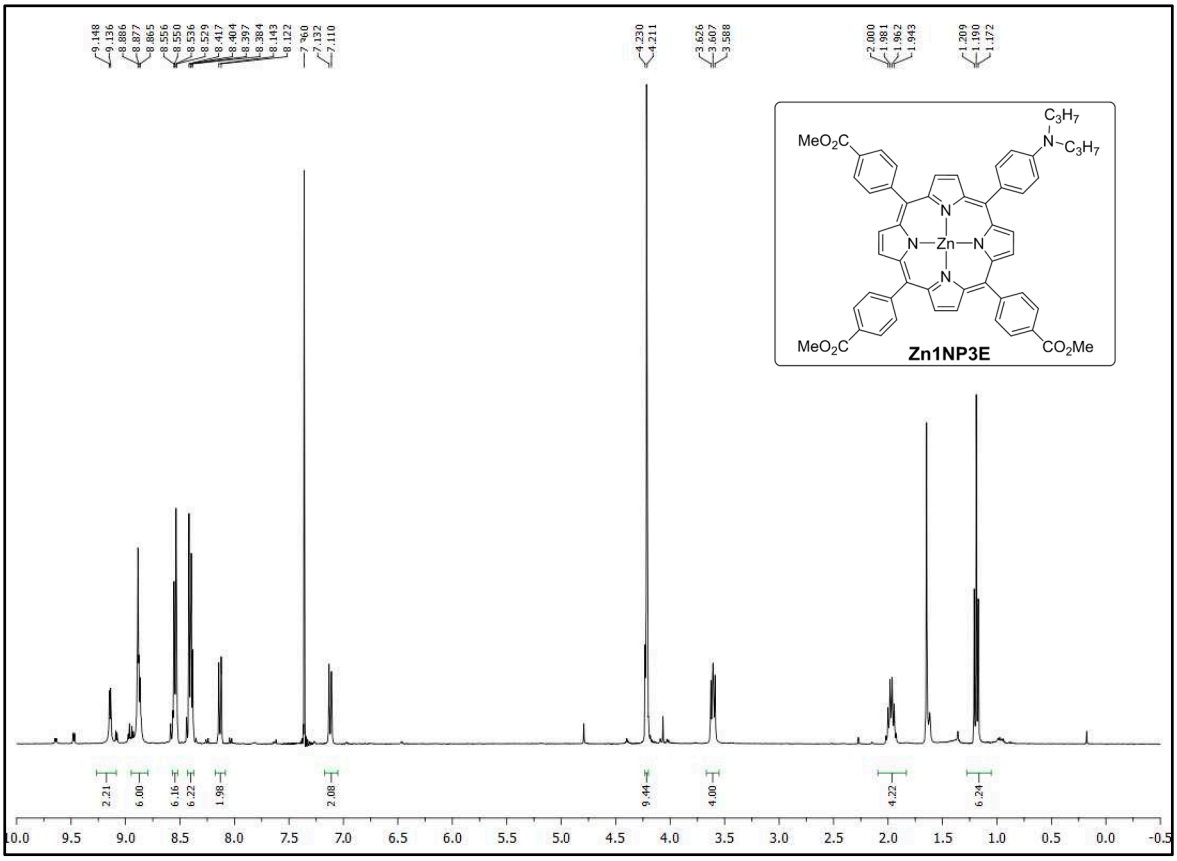


Figure S26. NMR spectrum of Zn_1NP_3E.

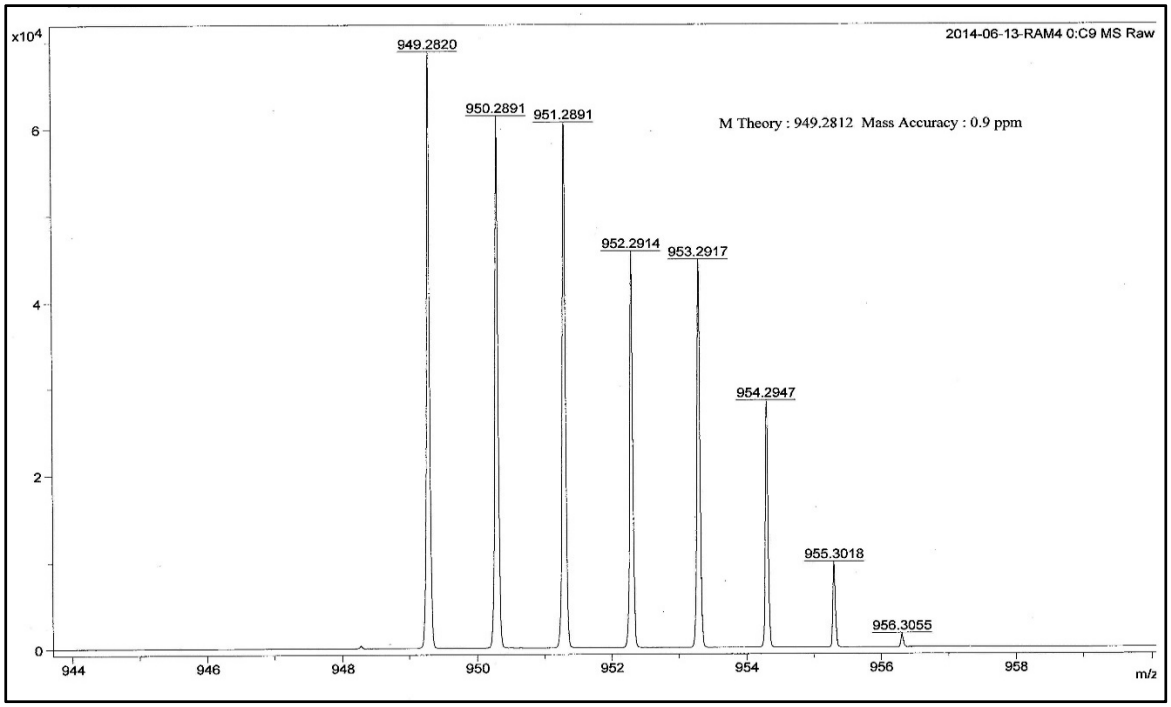


Figure S27. HRMS of Zn_1NP_3E.

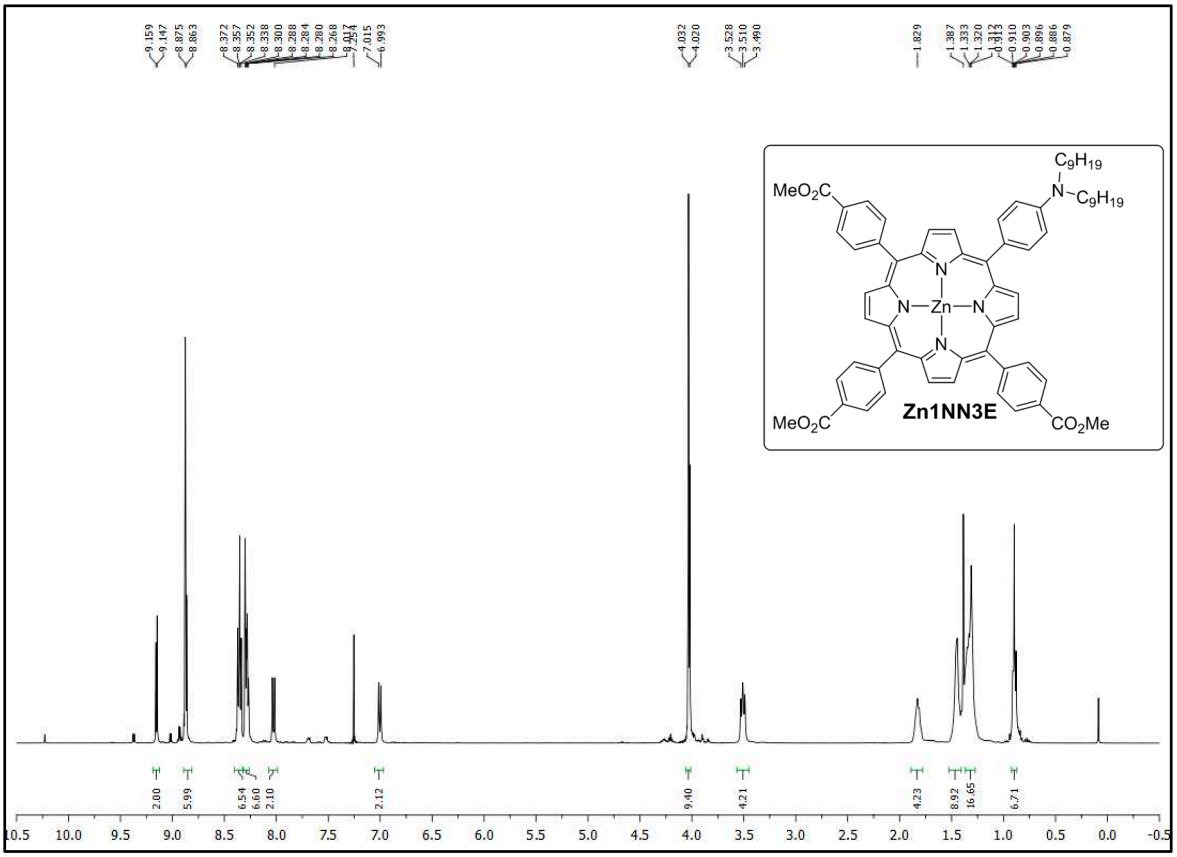


Figure S28. NMR spectrum of Zn_1NN_3E.

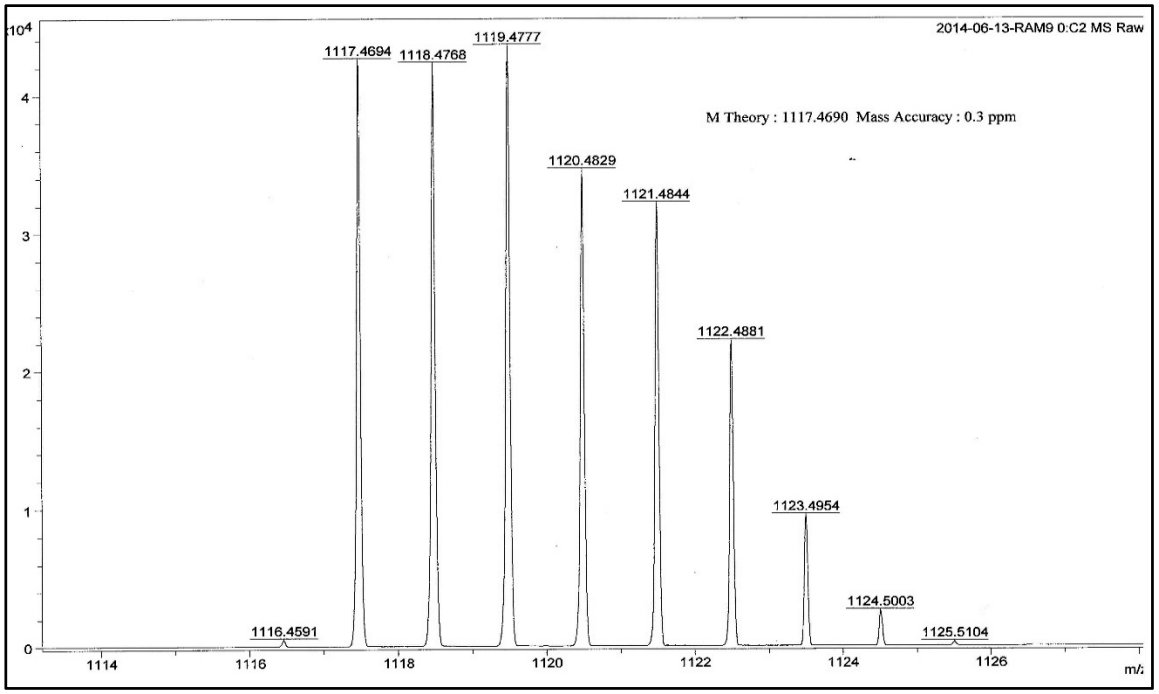


Figure S29. HRMS of Zn_1NN_3E.

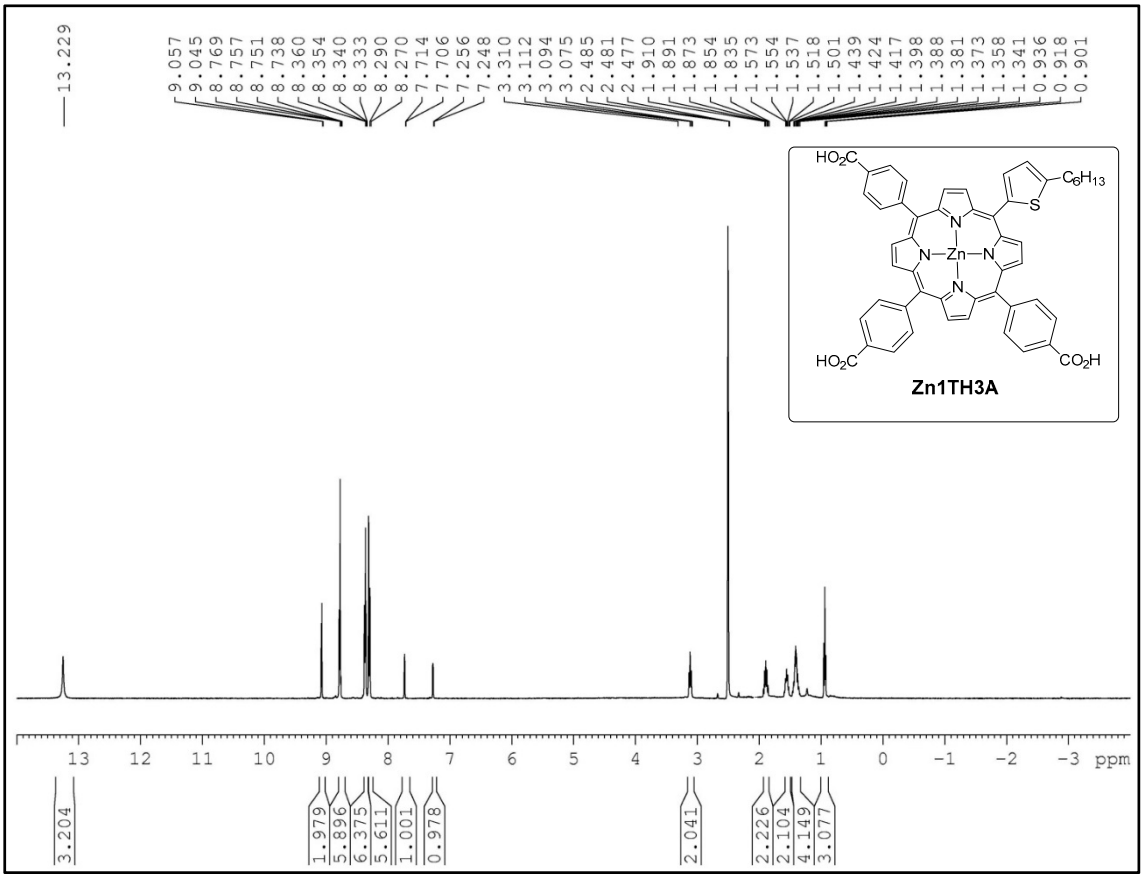


Figure S30. NMR spectrum of Zn_1TH_3A.

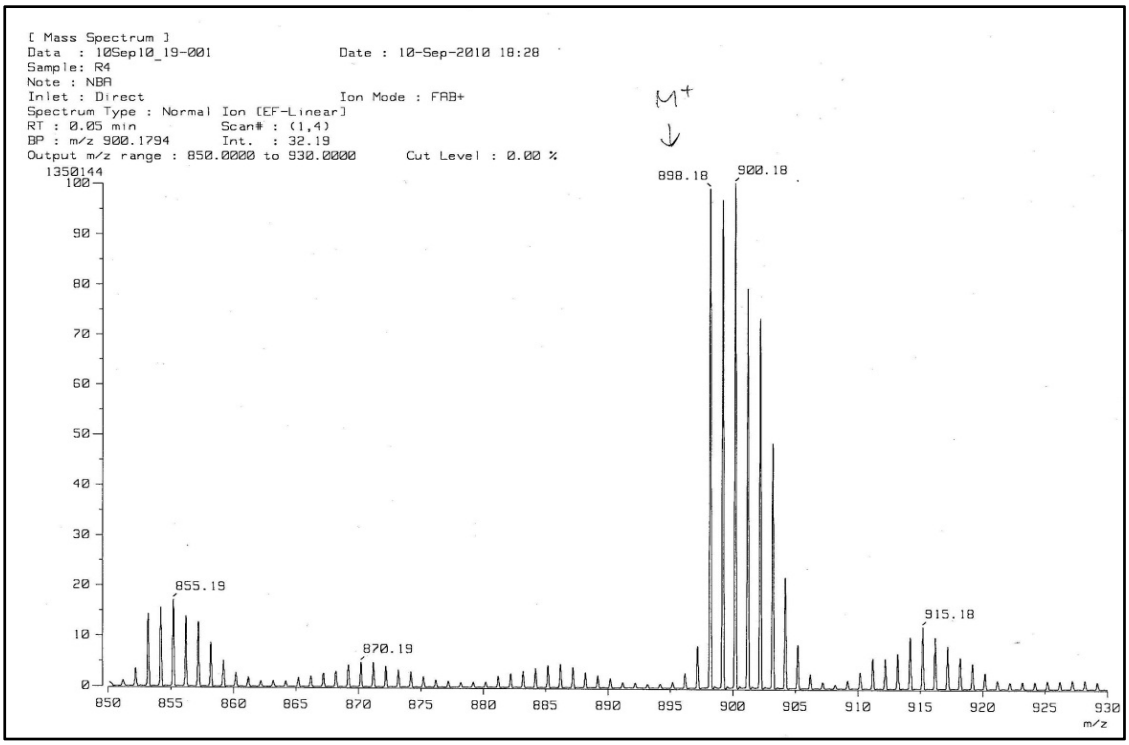


Figure S31. HRMS of Zn_1TH_3A.

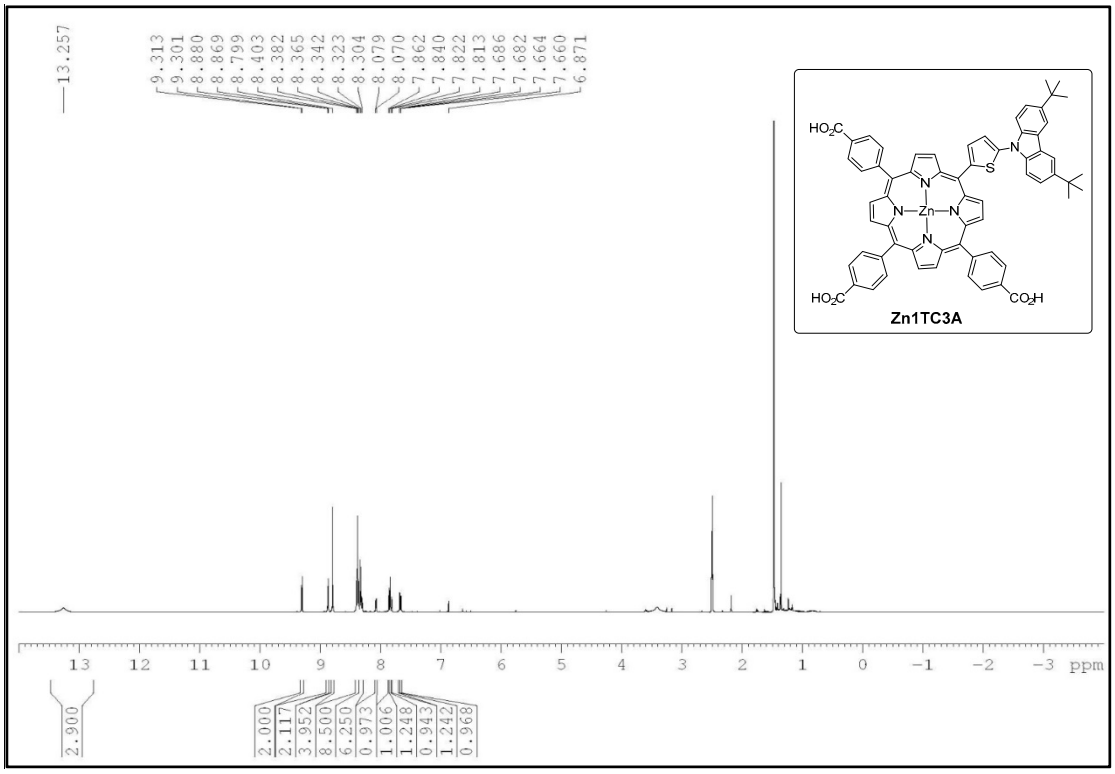


Figure S32. NMR spectrum of Zn_1TC_3A.

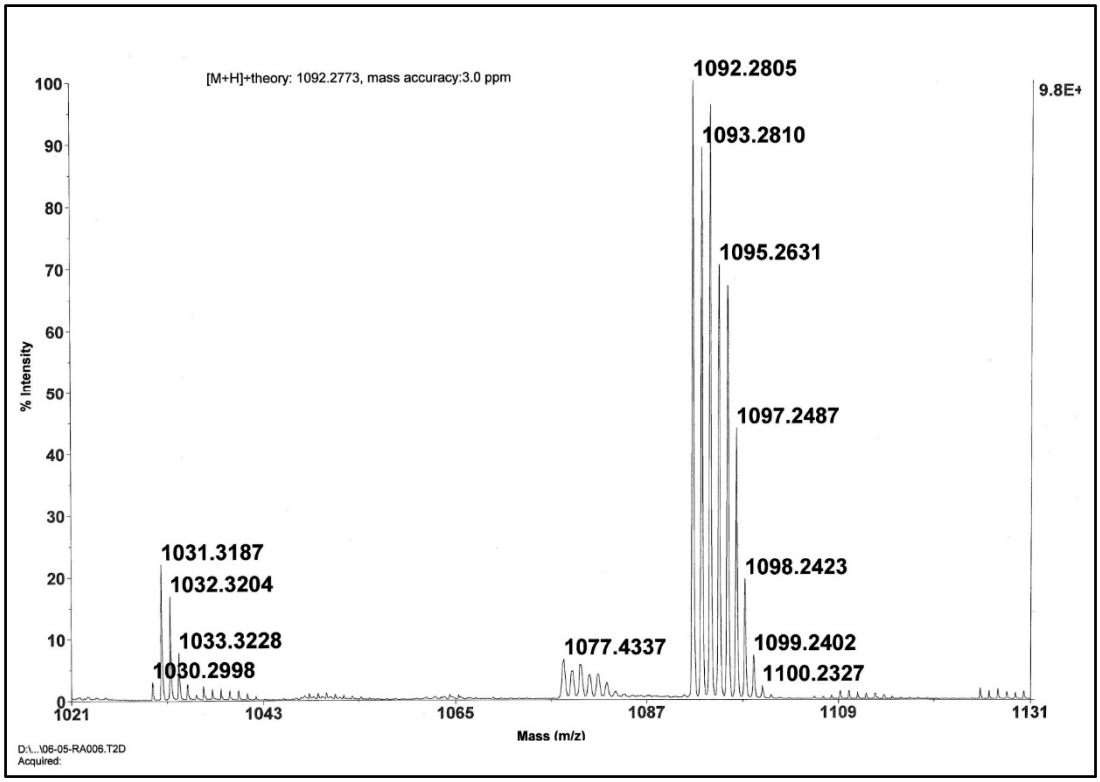


Figure S33. HRMS of Zn_1TC_3A.

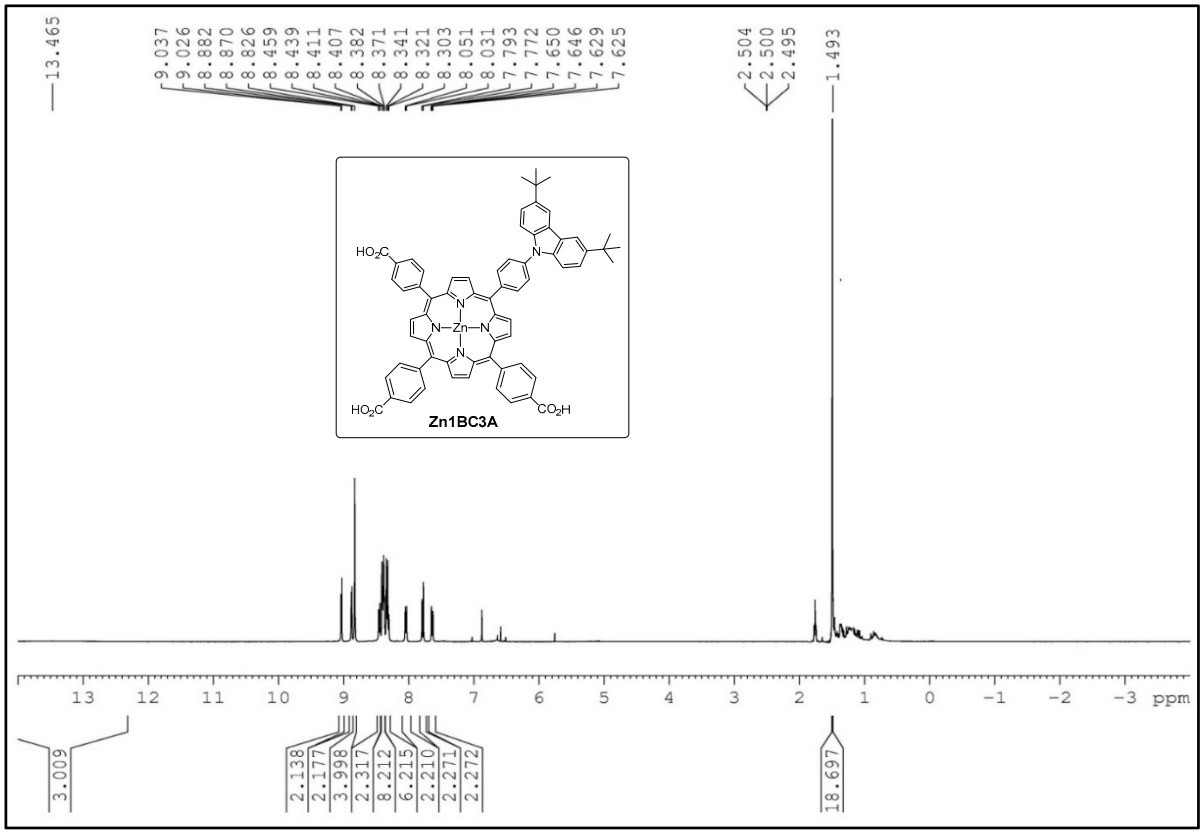


Figure S34. NMR spectrum of Zn_1BC_3A.

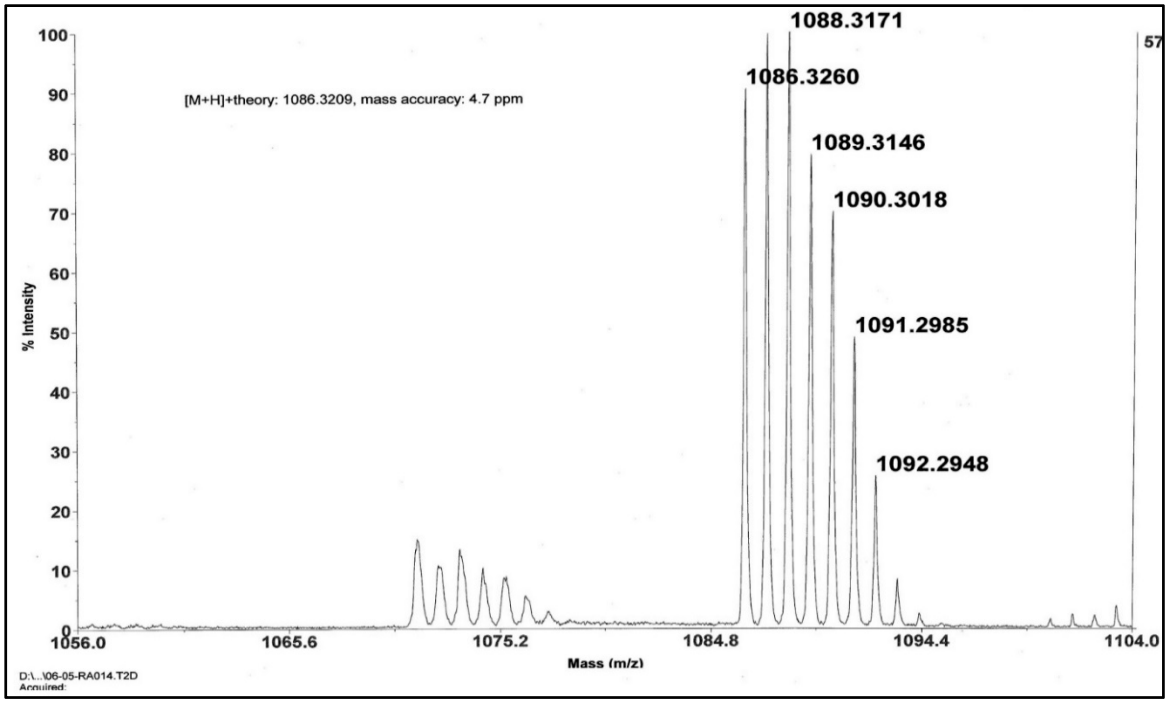


Figure S35. HRMS of Zn_1BC_3A.

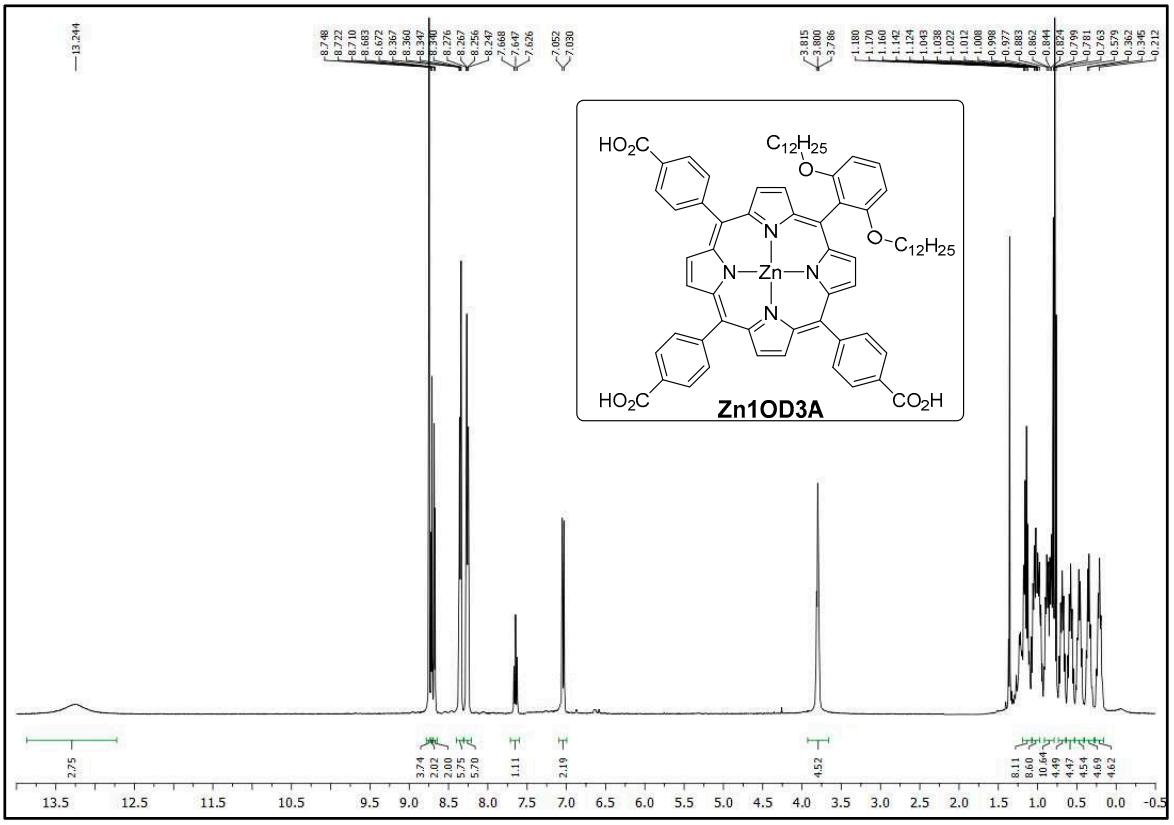


Figure S36. NMR spectrum of Zn_1OH_3A.

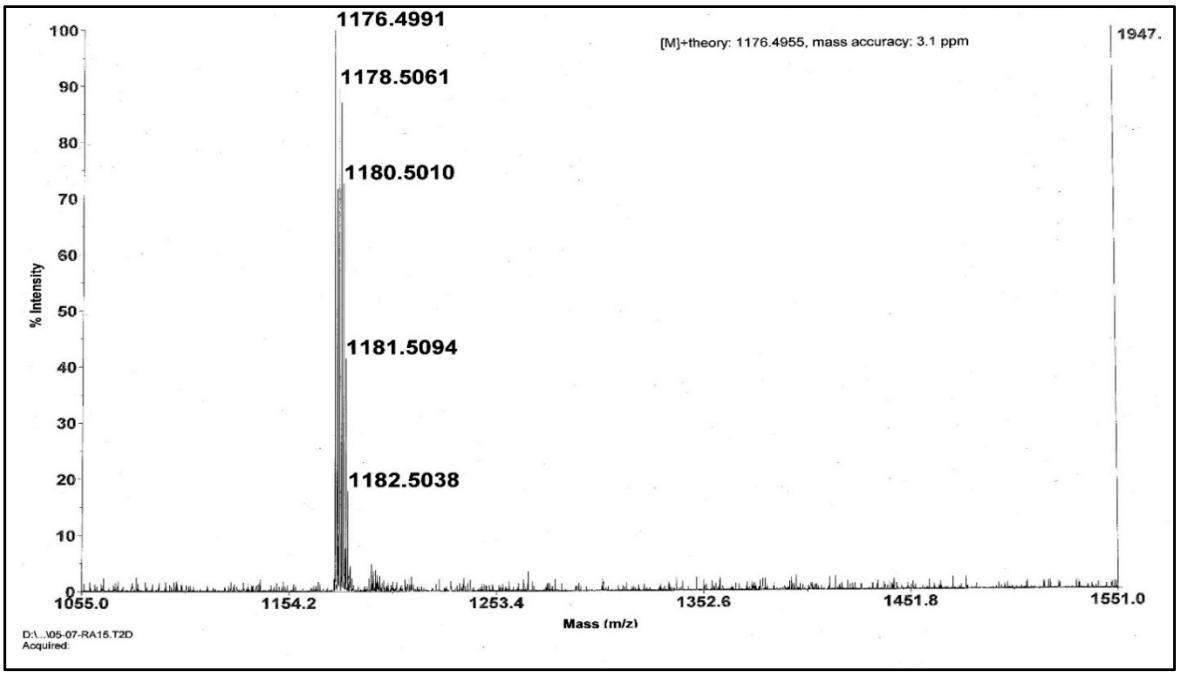
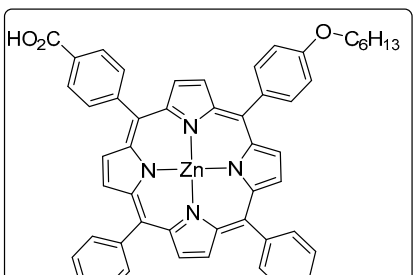


Figure S37. HRMS of Zn_1OD_3A.



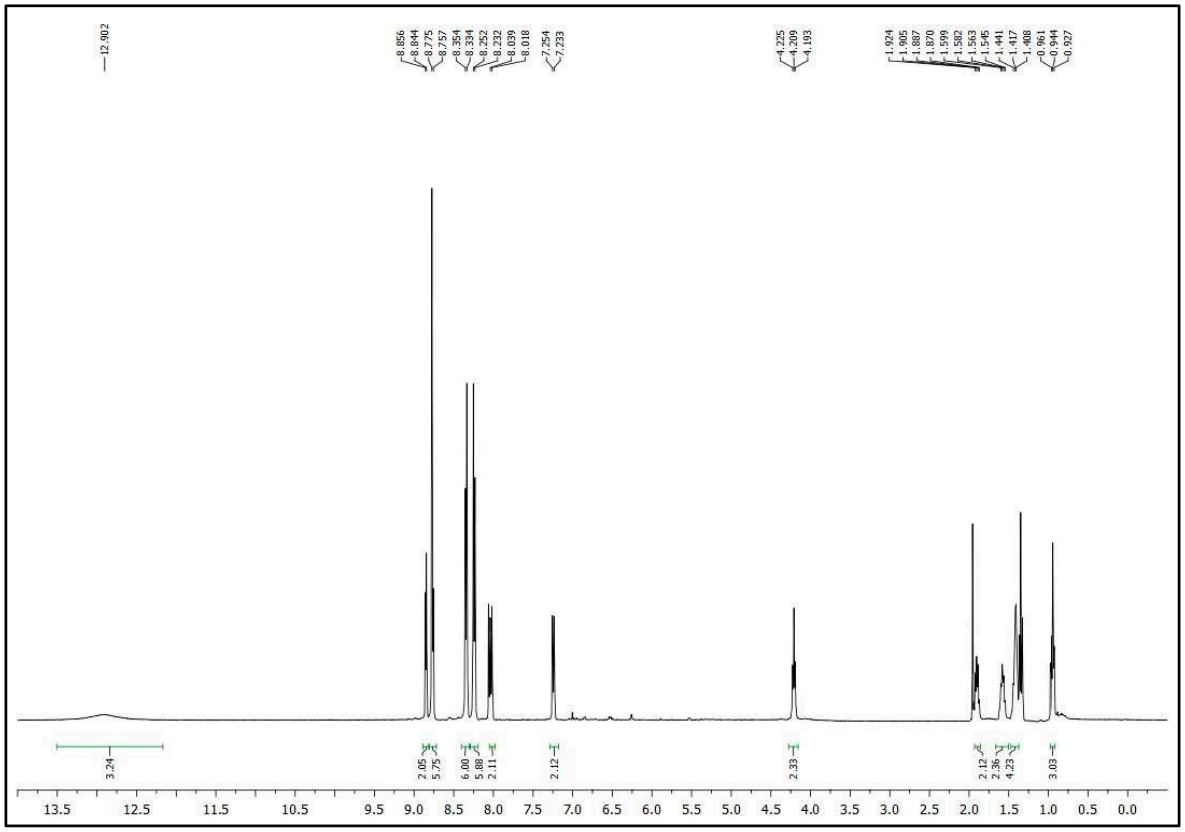


Figure S38. NMR spectrum of Zn_1OH_3A.

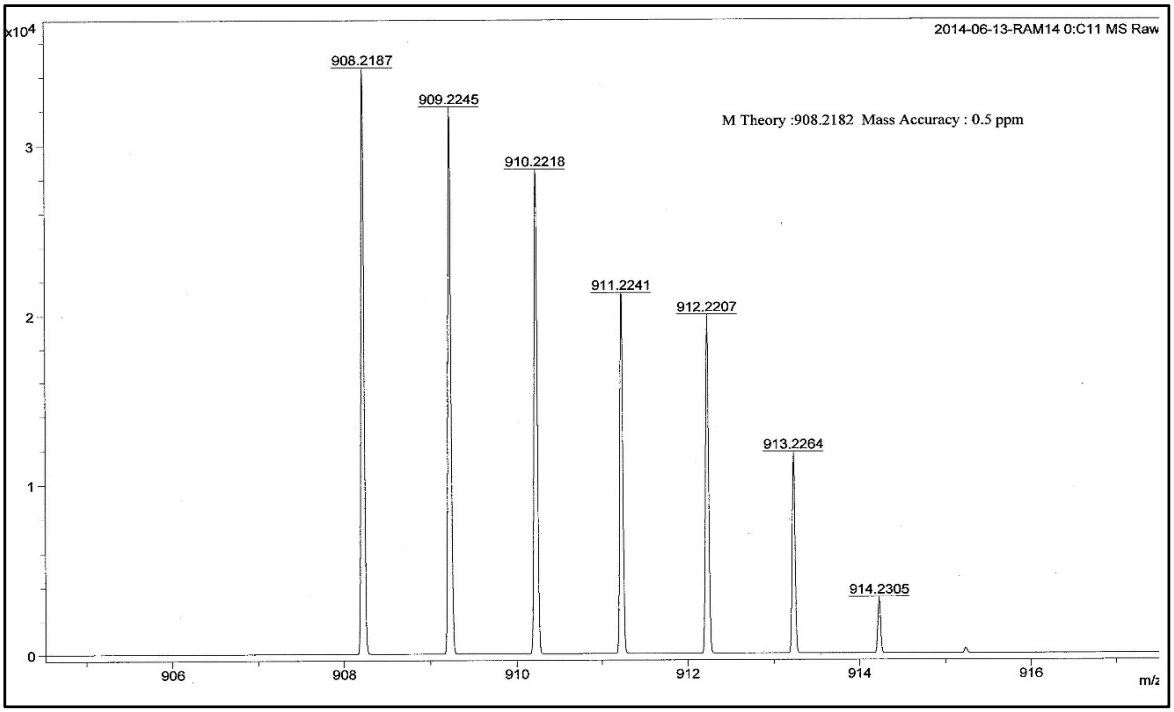


Figure S39. HRMS of Zn_1OH_3A.

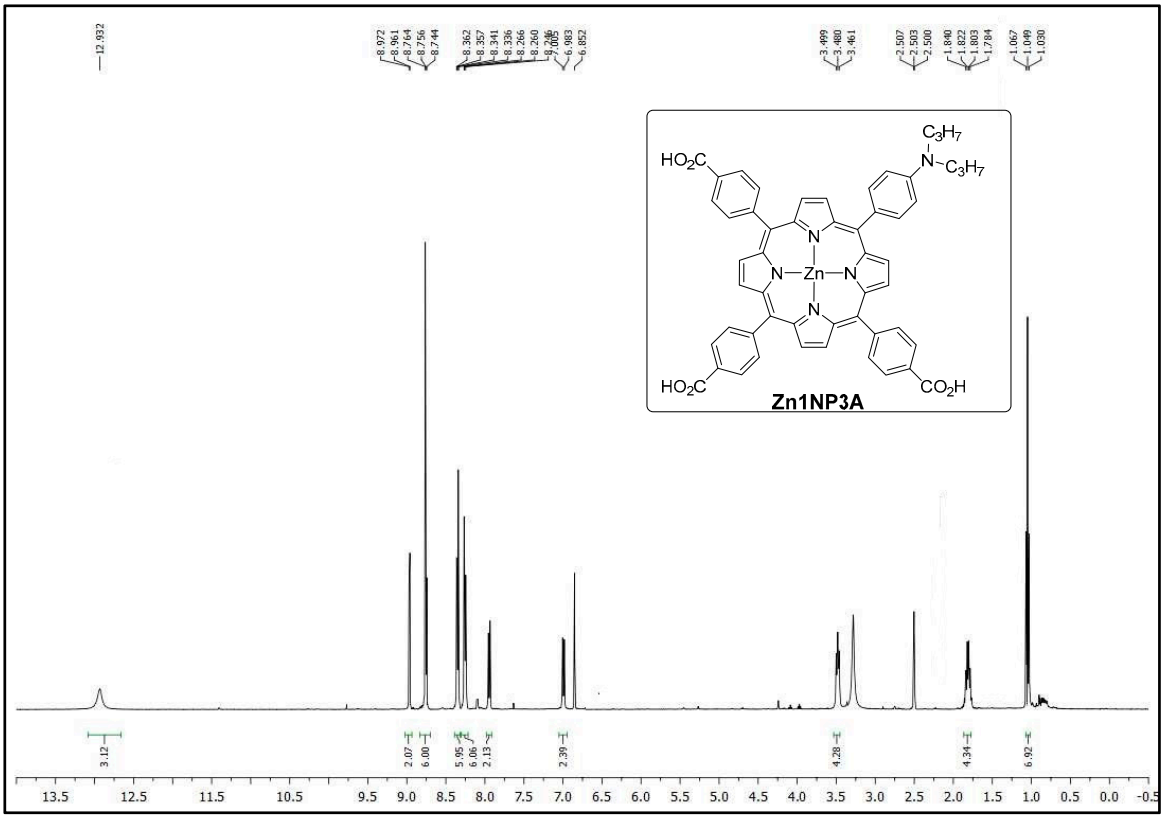


Figure S40. NMR spectrum of Zn_1NP_3A.

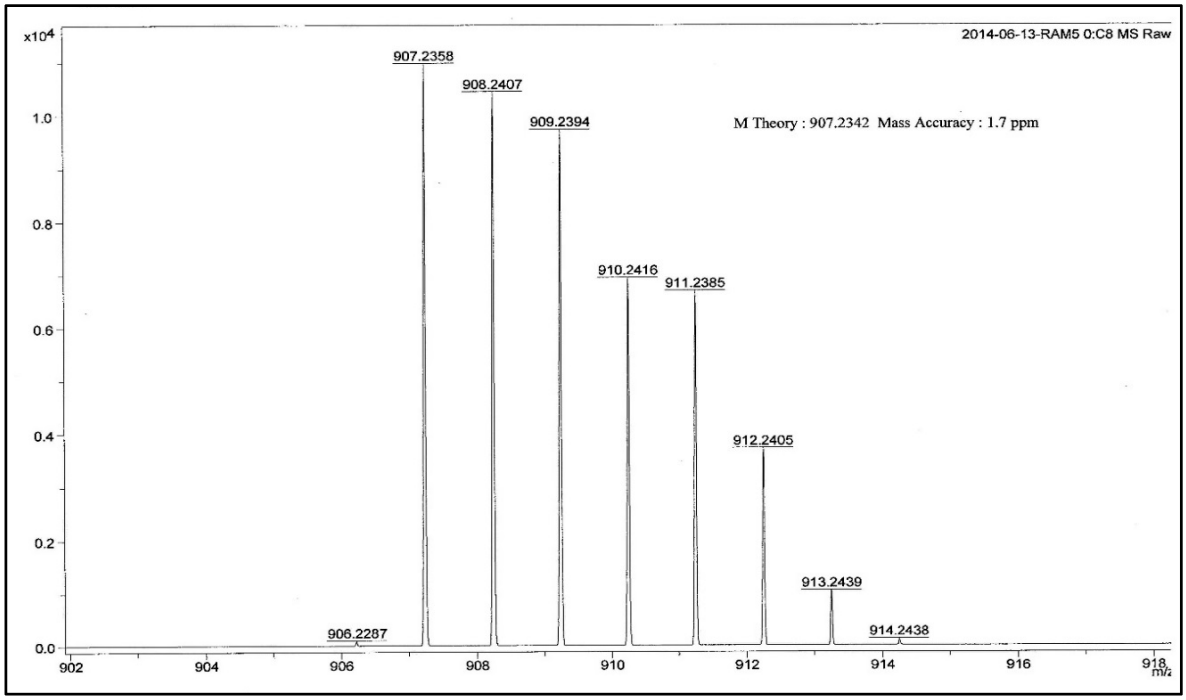


Figure S41. HRMS of Zn_1NP_3A.

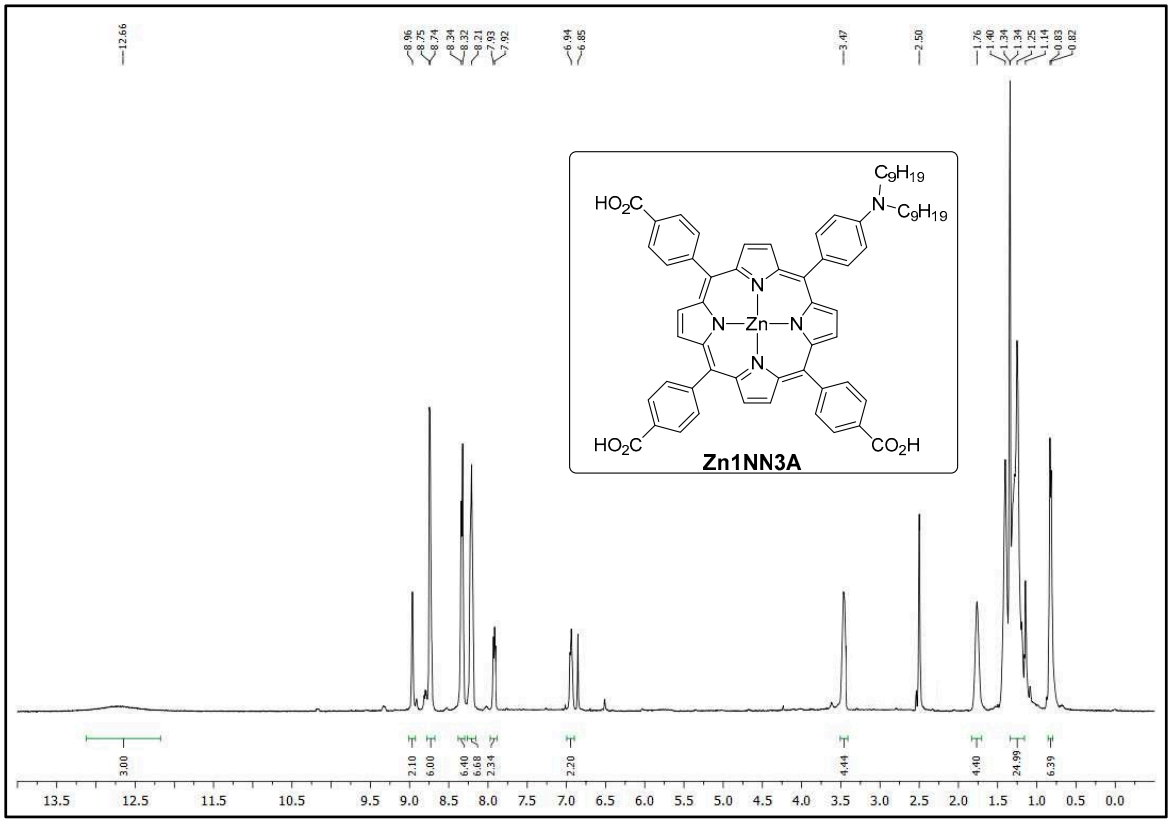


Figure S42. NMR spectrum of Zn_1NN_3A.

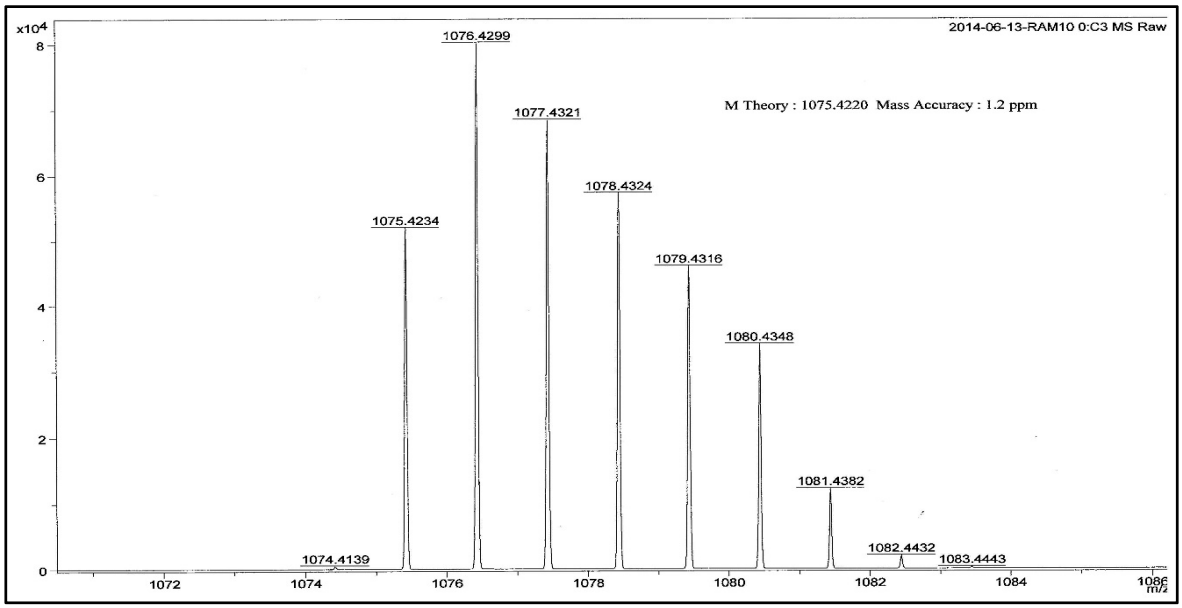


Figure S43. HRMS of Zn_1NN_3A.