Supporting information

Three Carboxyphenyl Groups Possessing Zinc Porphyrins: Efficient, Stable, and Cost-effective Sensitizers for Dye-Sensitized Solar Cells

Ram B. Ambre, Gao-Fong Chang, and Chen-Hsiung Hung*
Institute of Chemistry, Academia Sinica Nankang, Taipei, 115 Taiwan
Tel: +88627898570; E-mail:chhung@gate.sinica.edu.tw

No.	Table of contents	Page
1	Fig. S1. UV–visible absorption spectra of the 1D-π-3A porphyrins……...	S2
2	Fig. S2. UV–visible absorption spectra of the 1D-π-3A porphyrinson TiO_2.....	S2
3	Fig. S3. Cyclic votlammograms of the 1D-π-3A porphyrins …….	S3
4	Fig. S4. Molecular orbital diagrams of the studied porphyrins as obtained from DFT calculations ……..	S4
5	Fig S5. Absorption spectra of Zn1TPA3A, Zn1ND3A, Zn1NH3A and Zn3TPA1A that were adsorbed onto TiO_2 films after irradiation for 0, 5, and 30 min ……..	S5
6	Fig S6. ATR-FTIR spectra of (a) Zn1U3A and Zn1U3A/TiO_2 and (b) Zn1TPA3A and Zn1TPA3A/TiO_2……	S6
7	Fig S7. Possible modes of attachment of 1D-π-3A porphyrins onto TiO_2…….....	S6
8	Experimental Section……	S7
9	Synthesis of 1D-π-3A porphyrin sensitizers…….....	S10
10	NMR and HR-MS of 1D-π-3A porphyrin sensitizers……..	S17

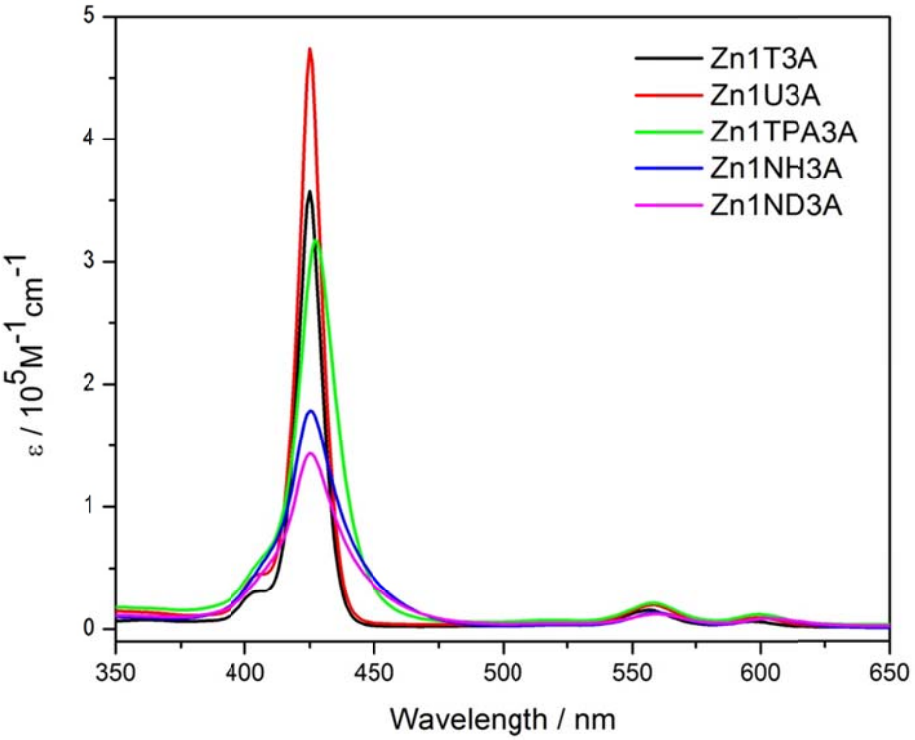


Fig. S1 UV–visible absorption spectra of the 1D-π-3A porphyrins.

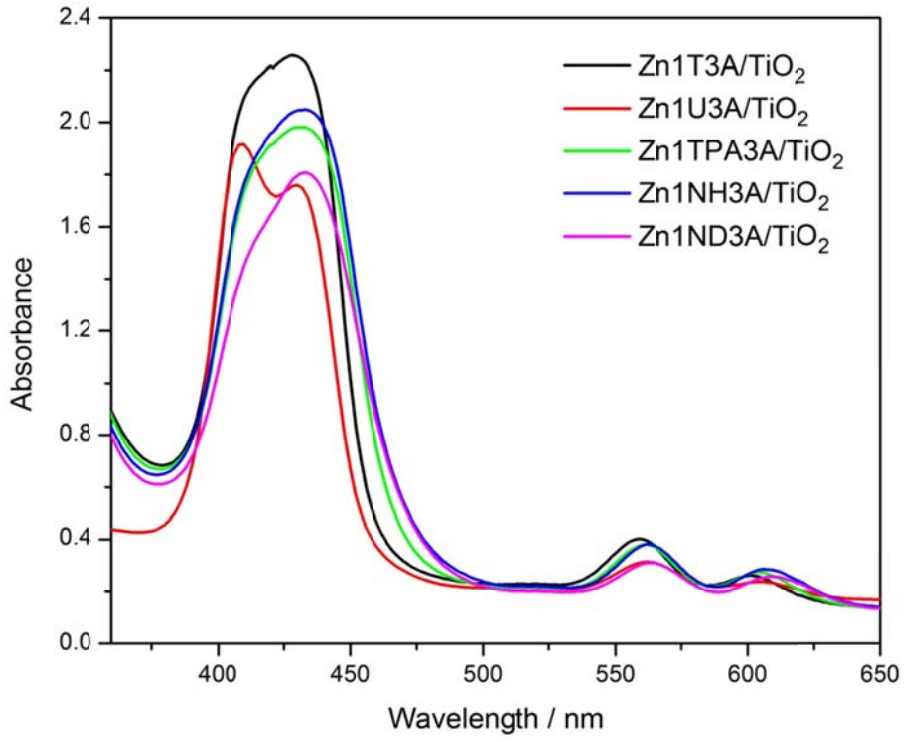


Fig. S2 UV–visible absorption spectra of the 1D-π-3A porphyrins on TiO_2.

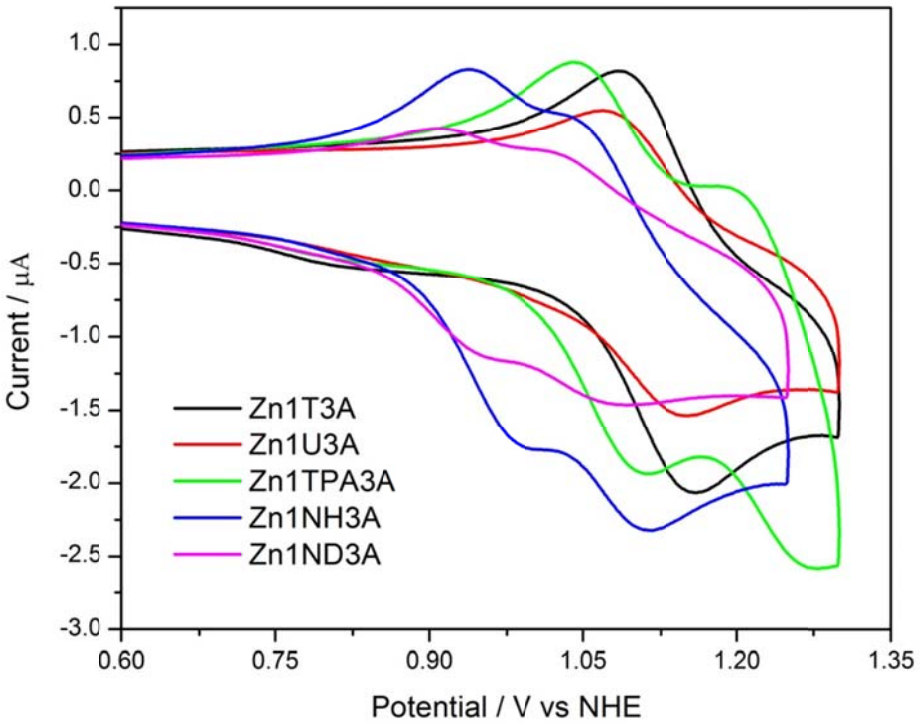


Fig. S3 Cyclic votlammograms of the 1D-π-3A porphyrins.

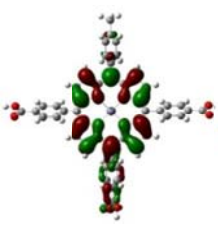
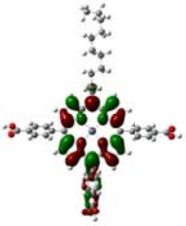
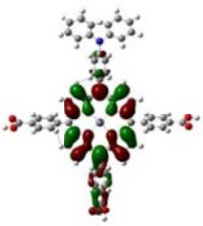
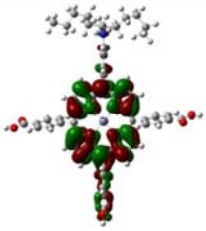
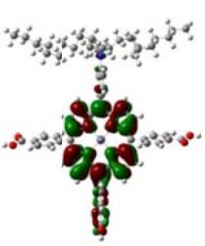
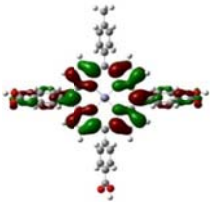
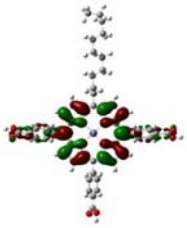
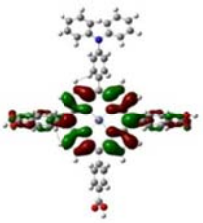
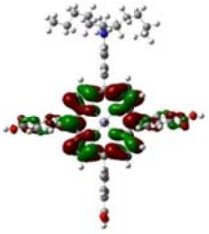
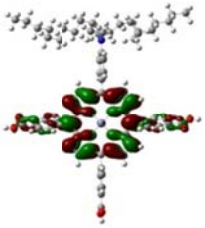
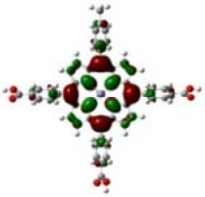
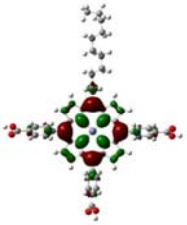
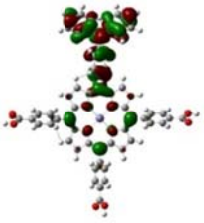
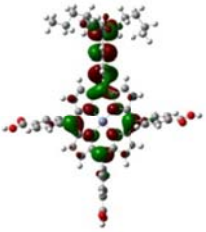
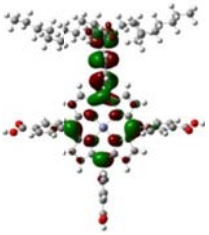
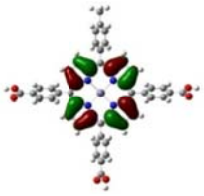
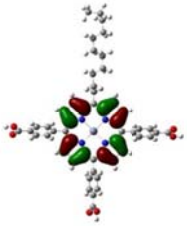
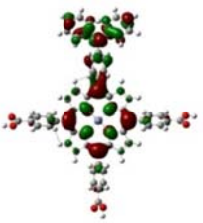
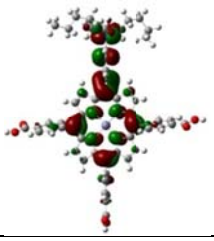
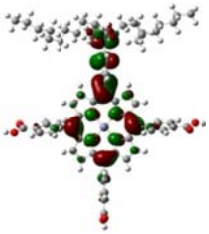
Dye	Zn1T3A	Zn1U3A	Zn1TPA3A	Zn1NH3A	Zn1ND3A
LUMO+1					
LUMO					
HOMO					
HOMO-1					

Fig. S4. Molecular orbital diagrams of the studied porphyrins as obtained from DFT calculations.

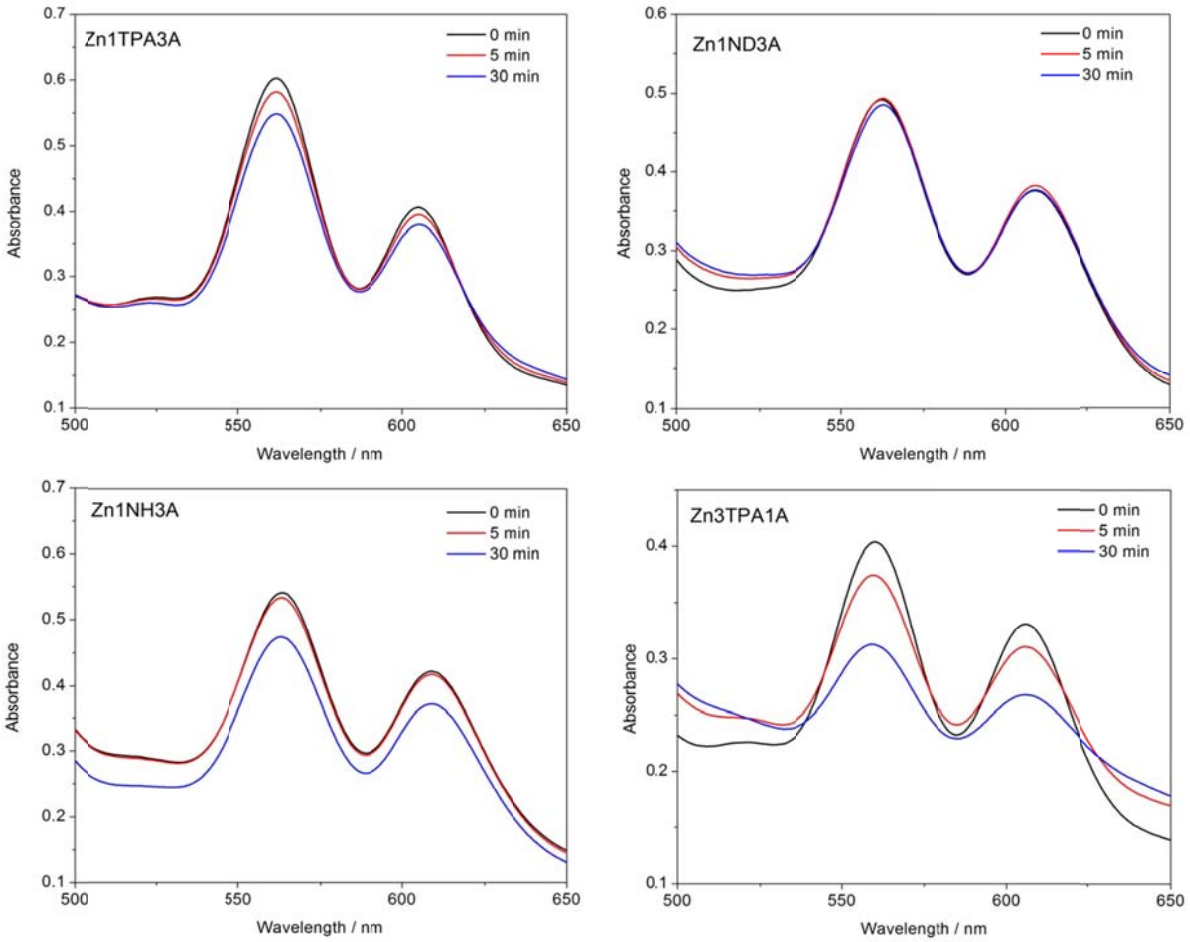
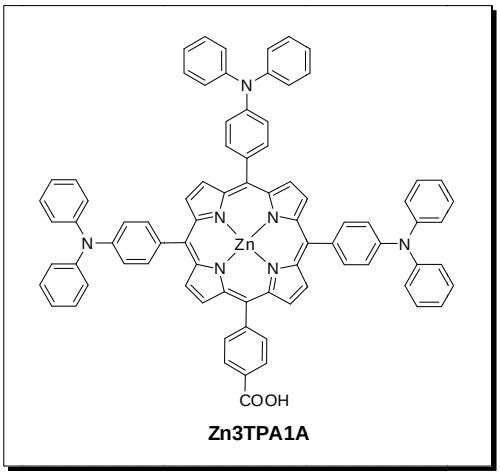


Fig S5. Absorption spectra of Zn1TPA3A, Zn1ND3A, Zn1NH3A and Zn3TPA1A that were adsorbed onto TiO_2 films after irradiation for 0, 5, and 30 min.



Structure of Zn3TPA1A

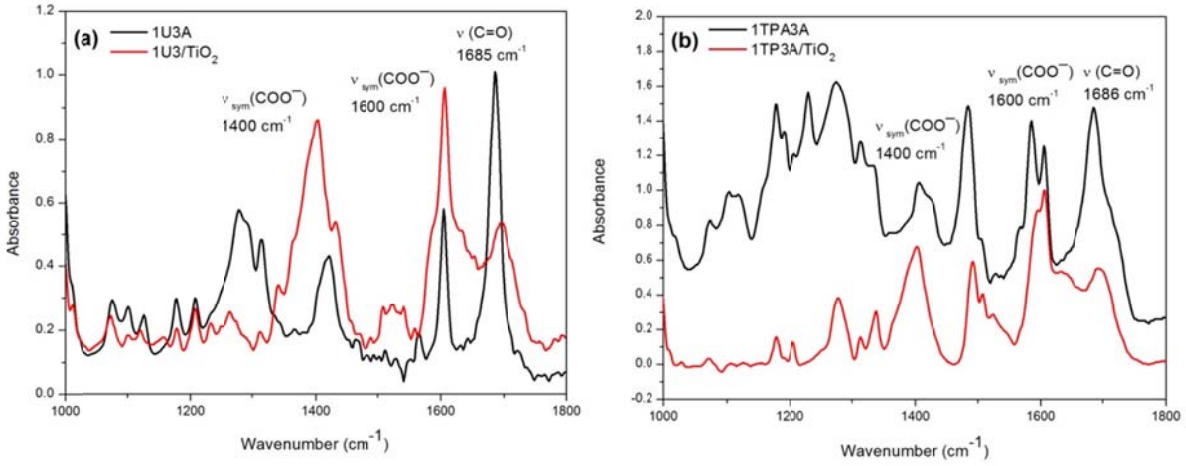


Fig S6 ATR-FTIR spectra of (a) Zn1U3A and Zn1U3A/TiO_2 and (b) Zn1TPA3A and Zn1TPA3A/TiO_2; the ATR-FTIR spectra of the porphyrins on TiO_2 are normalized for comparison.

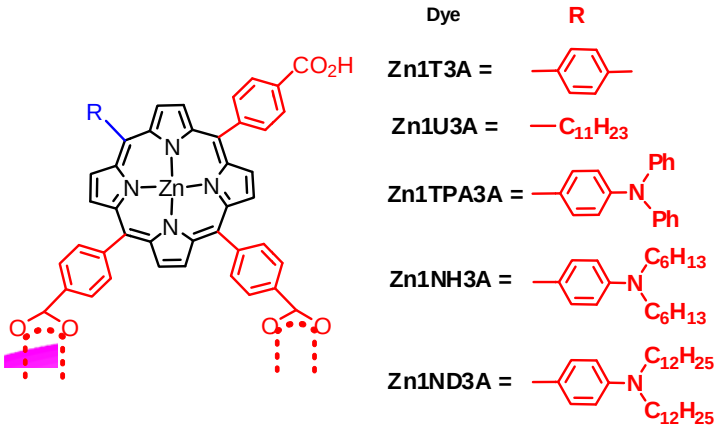


Fig S7. Possible modes of attachment of 1D-π-3A porphyrins onto TiO_2; for demonstration purpose only, the relative sizes of the molecules and nanoparticles are not correlated in real dimensions.

Experimental Section

Synthesis

All of the porphyrins were characterized by optical spectroscopy, ATR-FTIR, NMR spectroscopy, and HRMS. All of the chemicals were purchased from Acros Organics or Sigma Aldrich and used without further purification. ^{1}HNMR spectra were recorded on a Bruker 400MHz spectrometer in $CDCl_3$ (δ=7.26 ppm), or [D_6]DMSO (δ=2.50 ppm); Chemical shifts are reported in ppm. Coupling constants (J) are reported in Hz. The signals are described as s=singlet, d=doublet, t=triplet, or p=pentet. HRMS (FAB or ESI) was performed on a JMS-700 double-focusing mass spectrometer (JEOL, Tokyo, Japan). Flash chromatography was performed on silica gel (40-63 μm, Merck). Analytical TLC was performed on silica-gel plates (Merck). Melting points were recorded on a capillary melting-point apparatus (Electrothermal).

Optical Spectroscopy

UV/Vis absorption spectra of the porphyrins in THF and adsorbed onto TiO_2 electrodes were recorded on a JASCO V-670 UV/Vis/NIR spectrophotometer. For the absorption spectra of the thin films on TiO_2, TiO_2 films (area: 1×1 cm^2) were prepared with thicknesses of about 1 μm to obtain comparable shapes and peak positions. The films were immersed in 2×10^{-4} M solutions of the porphyrins in THF for 12 h and the films were rinsed with THF, dried, and the absorbance was measured. Steady-state fluorescence spectra were acquired on a Varian Cary Eclipse fluorescence spectrophotometer.

Cyclic Voltammetry

The CV measurements of all of the porphyrins were performed on a CHI 600D electrochemical analyzer (CH Instruments, Austin, TX, USA) in degassed THF with 0.1 M $TBAPF_6$ as a supporting electrolyte. The cell assembly consisted of a glassy carbon working electrode, Ag wire as a reference electrode, and platinum wire as the auxiliary electrode. A ferrocene/ferrocenium redox couple was used as an internal reference.

DFT Calculations

Geometry optimizations and the electronic structures of the porphyrins were performed by using DFT at the B3LYP level of theory with the 6-31G basis set in the Gaussian09 program package.

ATR-FTIR Measurements

ATR-FTIR spectra of the zinc porphyrins were recorded on a VERTEX 70 spectrometer with a Golden Gate diamond ATR accessory on solid powders of the porphyrin samples. For the preparation of the samples with zinc porphyrins adsorbed onto TiO_2, a 5×10^{-4} M solution of the porphyrin in THF was mixed with TiO_2 powder (5 mg) and left to stand for 12h. Afterwards, the excess solvent was dripped out by pipet. TiO_2 powder was washed twice with THF and dried invacuo and the obtained powder sample was used for the measurements. ATR-FTIR spectra of the zinc porphyrin that was adsorbed onto TiO_2 were recorded at a resolution of 4 cm^{-1} and averaged over 320 scans.

Photovoltaic Measurements

TiO_2 photoanode films were purchased from Yingkou Opvtech New Energy Co. Ltd. Liaoning, China. The films, which were prepared by using the screen-printing method, were composed of a transparent layer (thickness ≈12μm), a scattering layer (thickness ≈4μm), and a working area of 0.4×0.4 cm^2 and were used. The films were pretreated according to the following activation procedures before use: Heating at 100 °C for 22 min, at 110 °C for 60 min, at 450 °C for 68 min, at 500 °C 60 min, at 250 °C for 60 min, cooling at 80 °C and keeping at 80 °C before immersion. The TiO_2 films were immersed in a 2×10^{-4} M solution of the porphyrin in THF and a 2×10^{-4} M solution of CDCA at 50 °C. The dye-sensitized TiO_2 films were washed with THF, dried in hot air, and used as the working electrode. The counter electrode was prepared on an indium-doped tin-oxide glass substrate (typical size: 1.0×1.5 cm^2) by spin-coating a H_2PtCl_6/isopropanol solution through thermal decomposition at 380 °C for 0.5 h. To fabricate the DSSC device, the two electrodes were tightly clipped together into a sandwich-type cell that was spaced by a 40 μm film spacer. A thin layer of electrolyte, which contained 0.05 M I_2, 0.1m lithium iodide (LiI), 0.6 M dimethyl-propyl-benzimidiazole iodide (DMPII), and 0.6 M 4-tert-butylpyridine (TBP) in dry CH_3CN, was introduced into the space between the two electrodes. The photo-electrochemical characterizations on the solar cells were performed on an Oriel Class A solar simulator (Oriel 91195A, Newport Corp.). Photocurrent-voltage characteristics of the DSSCs were recorded on a potentiostat/galvanostat (CHI650B, CH Instruments, Inc.) at a light intensity of 100mWcm^{-2} and calibrated to an Oriel reference solar cell (Oriel 91150, Newport Corp.). The monochromatic quantum efficiency was recorded on a monochromator (Oriel 74100, Newport Corp.) under short-circuit conditions. The intensity of each wavelength was within the range 1-3mWcm^{M-2}.

Stability Study

For the stability study, TiO_2 thin films with areas of 1×1 cm^2 and thicknesses of 3-4 μm were used. The films were immersed in a 2×10^{-4} M solution of the porphyrin in THF for 0.5 h, dried, and the absorbance was measured. Then, the same films were irradiated under standard one sun illumination for 5 min and 30 min and the absorbance was measured again.

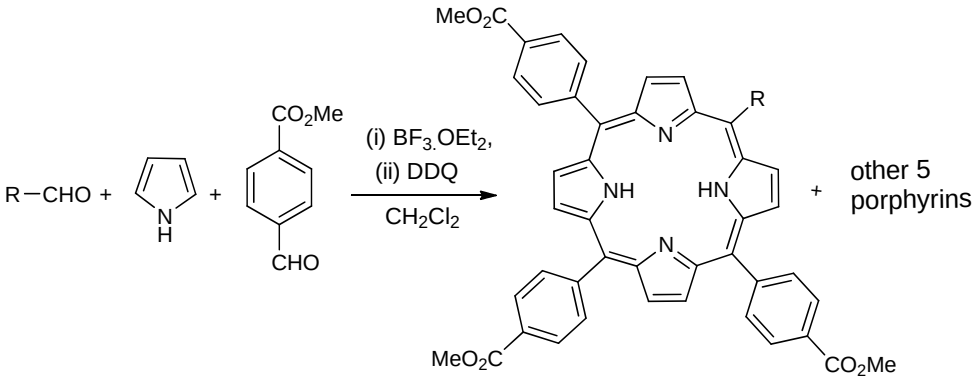
Synthesis of 1D-π-3A porphyrin sensitizers.

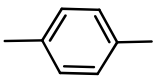
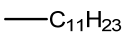
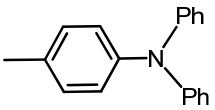
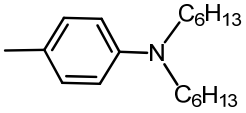
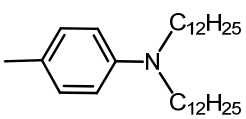
The zinc porphyrins used in this study Zn1T3A, Zn1U3A, Zn1TPA3A, Zn1NH3A and Zn1ND3A were synthesized in three steps, (I) mixed condensation, (II) Zinc metalation, (III) Base hydrolysis. For detail synthetic procedures please follow our previous article, R. B. Ambre, G.-F. Chang, M. R. Zanwar, C.-F. Yao, E. W.-G. Diau and C.-H. Hung, *Chem. Asian J.* **2013.**

(I) 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 1T3E, 1U3E, 1TPA3E, 1NH3E, and 1ND3E obtained from each separate reaction are reported in Table S1.

Table S1. Mixed condensation[a]

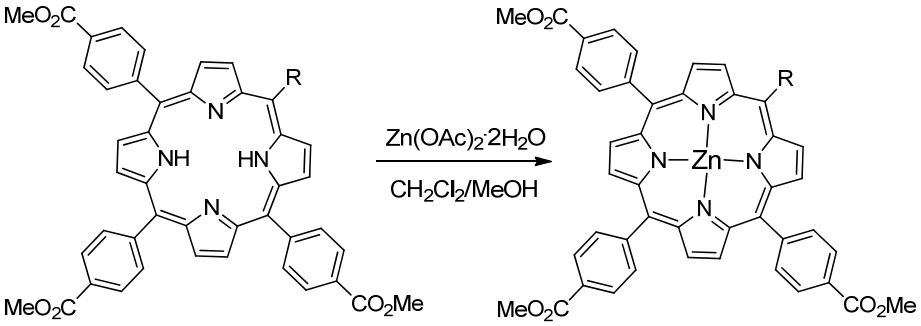


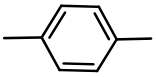
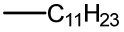
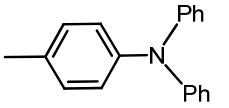
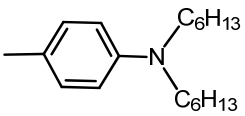
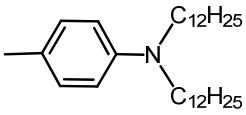
1X3E	R	Yield (%)
1T3E		6.68
1U3E		2.65
1TPA3E		9.70
1NH3E		5.41
1ND3E		2.33

(II) 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 Zn1T3E, Zn1U3E, Zn1TPA3E, Zn1NH3E, and Zn1ND3E 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 UV–visible spectra the zinc porphyrins shows single strong Soret band and two moderate Q bands.

Table S2. Zn metalation[a]

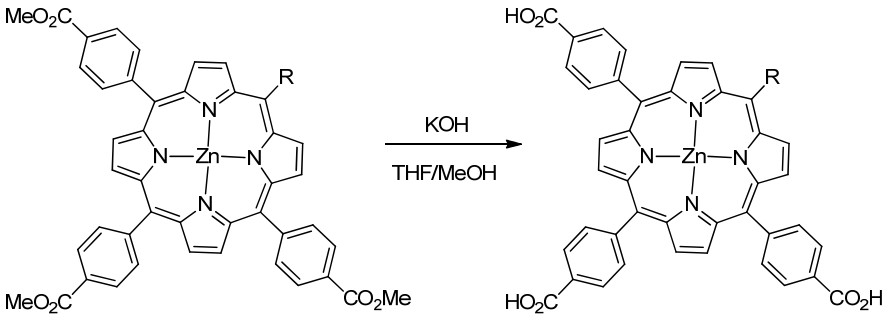


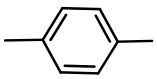
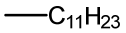
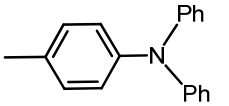
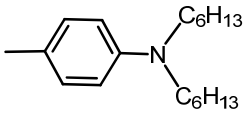
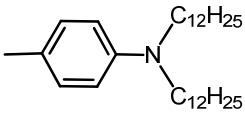
Zn1X3E	R	Yield (%)
Zn1T3E		91
Zn1U3E		90
Zn1TPA3E		99
Zn1NH3E		92
Zn1ND3E		89

(III) 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 Zn1T3A, Zn1U3A, Zn1TPA3A, Zn1NH3A, and Zn1ND3A are listed in Table S3. 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[a]



Zn1X3A (Dye)	R	Yield (%)
Zn1T3A		97
Zn1U3A		99
Zn1TPA3A		98
Zn1NH3A		99
Zn1ND3A		90

Characterization Data;

5,10,15-tris(4-methoxycarbonylphenyl)20-(4-methylphenyl)porphyrin (1T3E). mp > 300 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.91 (d, J = 4.7 Hz, 2H, β-py), 8.81 (m, 4H, β-py), 8.79 (d, J = 4.8 Hz, 2H, β-py), 8.44 (d, J = 8.2 Hz, 6H, Ar-H), 8.30 (d, J = 8.2 Hz, 6H, Ar-H), 8.09 (d, J = 8.1, 2H, Ar-H), 7.56 (d, J = 7.7 Hz, 2 H, Ar-H), 4.11 (s, 9H, COOMe), 2.71 (s, 3 H, Me), -2.71 (s, 2H, NH); IR (Neat, cm^{-1}): 3307 (N-H), 1719 (C=O), 1605, 1434, 1370,1275, 1180, 1100, 1019, 964, 797; λ_{abs}/nm (CH_2Cl_2): 420, 516, 552, 590, 646; HRMS-ESI calcd for $C_{51}H_{38}N_4O_6$ ($[M+H]^+$): 803.2870, found 803.2877.

5,10,15-tris(4-methoxycarbonylphenyl)20-(undecyl)porphyrin (1U3E). mp > 300 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.48 (d, J = 4.8 Hz, 2H, β-py), 8.86 (d, J = 4.7 Hz, 2H, β-py), 8.76 (s, 4H, β-py), 8.46- 8.42 (m, 6H, Ar-H), 8.30-8.26 (m, 6H, Ar-H), 4.95 (t, J = 8.0, 2H, CH_2), 4.14 (s, 6H, COOMe), 4.11 (s, 3H, COOMe), 2.53 (p, J = 7.4 Hz, 2H, CH_2) 1.78 (p, J = 7.3 Hz, 2H, CH_2), 1.51 (p, J = 7.4 Hz, 2H, CH_2), 1.37-1.26 (m, 12 H, CH_2), 0.87 (t, J = 6.8 Hz, 3H, CH_3), -2.73 (s, 2H, NH); IR (Neat, cm^{-1}): 3313 (N-H), 1719 (C=O), 1606, 1434, 1271, 1226, 1192, 1177, 1099, 1021, 962; λ_{abs}/nm (CH_2Cl_2): 418, 516, 552, 592, 648; HRMS-ESI calcd for $C_{55}H_{54}N_4O_6$ ($[M+H]^+$): 867.4122, found 887.4146.

5,10,15-tris(4-methoxycarbonylphenyl)20-(4-diphenylaminophenyl)porphyrin (1TPA3E). mp > 300 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.09 (d, J = 4.7 Hz, 2H, β-py), 8.83 (d, J = 4.8, 2H, β-py), 8.80 (s, 4H, β-py), 8.86-8.43 (m, 6H, Ar-H), 8.32-8.28 (m, 6H, Ar-H), 8.06 (d, J = 8.3 Hz, 2H, Ar-H), 7.45 (d, J = 8.3 Hz, 2H, Ar-H), 7.42-7.13 (m, 8H, Ar-H), 7.17-7.40 (m, 2H, Ar-H), 4.12 (s, 6H, COOMe), 4.11 (s, 3H, COOMe), -2.75 (s, 2H, NH); IR (Neat, cm^{-1}): 3313 (N-H), 1719 (C=O), 1605, 1590, 1489, 1401, 1311, 1270, 1178, 982, 963, 759, 712; λ_{abs}/nm (CH_2Cl_2): 418, 518, 556, 592, 650, 706; HRMS-ESI calcd for $C_{62}H_{45}N_5O_6$ ($[M+H]^+$): 956.3448, found 956.3452.

5,10,15-tris(4-methoxycarbonylphenyl)20-(4-N,N-dihexylaniline)porphyrin (1NH3E). mp > 300 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.06 (d, J = 4.7 Hz, 2H, β-py), 8.83-8.76 (m, 6H, β-py), 8.46-8.43 (m, 6H, Ar-H), 8.32-8.29 (m, 6H, Ar-H), 8.05 (d, J = 8.4 Hz, 2H, Ar-H), 7.02 (d, J = 8.6 Hz, 2H, Ar-H), 4.12 (s, 6H, COOMe), 4.11 (s, 3H, COOMe), 3.52 (t, J = 7.4 Hz, 4H, CH_2), 1.84 (p, J = 7.2 Hz, 4H, CH_2), 1.47-1.41 (m, 12H, CH_2), 0.97 (t, J = 6.9 Hz, 6H, CH_3), -2.67 (s,

2H, NH); IR (Neat, cm^{-1}): 3319 (N-H), 1724 C=O), 1604, 1515, 1467, 1434, 1367, 1272, 1191, 1097 1020, 964, 964, 798, 761, 732; λ_{abs}/nm (CH_2Cl_2): 416, 515, 557, 653, 731; HRMS-ESI calcd for $C_{62}H_{61}N_5O_6$ ($[M+H]^+$): 972.4700, found 972.4734.

5,10,15-tris(4-methoxycarbonylphenyl)20-(4-N,N-didodecylaniline)porphyrin (1ND3E). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.06 (d, J = 4.7 Hz, 2H, β-py), 8.80-8.78 (m, 6H, β-py), 8.46-8.43 (m, 6H, Ar-H), 8.46-8.29 (m, 6H, Ar-H), 8.04 (d, J = 8.5 Hz, 2H, Ar-H), 7.02 (d, J = 8.6 Hz, 2H, Ar-H), 4.12 (s, 6H, COOMe), 4.11 (s, 3H, COOMe), 3.52 (t, J = 6.9 Hz, 4H, CH_2), 1.84 (m, 4H, CH_2), 1.47-1.27 (m, 36H, CH_2), 0.91-0.86 (m, 6H, CH_3), -2.67 (s, 2H); IR (Neat, cm^{-1}): 3315 (N-H), 1718 (C=O), 1604, 1513, 1433, 1400, 1271, 1190, 1099, 1020, 962, 796, 759, 720; λ_{abs}/nm (CH_2Cl_2): 416, 516, 567, 655, 731; HRMS-ESI calcd for $C_{74}H_{85}N_5O_6$ ($[M+H]^+$): 1140.6578, found 1140.6624.

5,10,15-tris(4-methoxycarbonylphenyl)20-(4-methylphenyl)porphyrinato zinc(II) (Zn1T3E). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.00 (d, J = 4.9 Hz, 2H, β-py), 8.90 (s, 4H, β-py), 8.89 (d, J = 5.2 Hz, 2H, β-py), 8.42 (d, J = 8.2 Hz, 6H, Ar-H), 8.29 (d, J = 7.8 Hz, 6H, Ar-H), 8.09 (d, J = 7.5, 2H, Ar-H), 7.56 (d, J = 7.6 Hz, 2H, Ar-H), 4.09 (s, 9H, COOMe), 2.71 (s, 3H, Me); IR (Neat, cm^{-1}): 1720 (C=O), 1701 (C=O), 1604, 1432, 1269, 1179, 1100, 1070, 996, 967, 793; λ_{abs}/nm (CH_2Cl_2): 422, 550, 590; HRMS-FAB calcd for $C_{51}H_{36}N_4O_6Zn$ ($[M^+]$): 864.1926, found 864.1919.

5,10,15-tris(4-methoxycarbonylphenyl)20-(undecyl)porphyrinato zinc(II) (Zn1U3E). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.48 (d, J = 4.8 Hz, 2H, β-py), 8.87 (d, J = 4.6 Hz, 2H, β-py), 8.84 (s, 4H, β-py), 8.38- 8.34 (m, 6H, Ar-H), 8.26-8.24 (m, 6H, Ar-H), 4.89 (t, J = 8.1, 2H, CH_2), 4.06 (s, 6H, COOMe), 4.03 (s, 3H, COOMe), 2.52 (p, J = 7.4 Hz, 2H, CH_2) 1.82 (p, J = 7.3 Hz, 2H, CH_2), 1.51 (p, J = 7.4 Hz, 2H, CH_2), 1.41-1.30 (m, 12 H, CH_2), 0.86 (t, J = 8.2 Hz, 3H, CH_3); IR (Neat, cm^{-1}): 1721 (C=O), 1701 (C=O), 1605, 1270, 1207, 1112, 1105, 997, 821; λ_{abs}/nm (CH_2Cl_2): 420, 548, 592; HRMS- MALDI-TOF calcd for $C_{55}H_{52}N_4O_6Zn$ ($[M+H]^+$): 929.3257, found 929.3271.

5,10,15-tris(4-methoxycarbonylphenyl)20-(4-diphenylaminophenyl)porphyrinato zinc(II) (Zn1TPA3E). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.13 (d, J = 4.7 Hz, 2H, β-py), 8.92 (d, J = 4.8, 2H, β-py), 8.89 (s, 4H, β-py), 8.41-8.38 (m, 6H, Ar-H), 8.31-8.27 (m, 6H, Ar-H),

8.06 (d, J = 8.3 Hz, 2H, Ar-H), 7.45 (d, J = 8.3 Hz, 2H, Ar-H), 7.41-7.40 (m, 8H, Ar-H), 7.15-7.12 (m, 2H, Ar-H), 4.07 (s, 6H, COOMe), 4.06 (s, 3H, COOMe); IR (Neat, cm^{-1}): 1720 (C=O), 1703 (C=O), 1605, 1590, 1489, 1401, 1307, 1270, 1177, 1023, 996, 867, 762; λ_{abs}/nm (CH_2Cl_2): 422, 516, 550, 592; HRMS-FAB calcd for $C_{62}H_{43}N_5O_6Zn$ ([M^+]): 1017.2507, found 1017.2528.

5,10,15-tris(4-methoxycarbonylphenyl)20-(N,N-dihexylaniline)porphyrinato zinc(II) (Zn1NH3E). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.15 (d, J = 4.6 Hz, 2H, β-py), 8.89-8.87 (m, 6H, β-py), 8.38-8.35 (m, 6H, Ar-H), 8.30-8.27 (m, 6H, Ar-H), 8.03 (d, J = 8.5 Hz, 2H, Ar-H), 7.00 (d, J = 8.6 Hz, 2H, Ar-H), 4.04 (s, 6H, COOMe), 4.03 (s, 3H, COOMe), 3.51 (t, J = 7.5 Hz 4H, CH_2), 1.83 (p, J = 7.8 Hz, 4H, CH_2), 1.46-1.41 (m, 12H, CH_2), 0.96 (t, J = 6.9 Hz, 6H, CH_3); IR (Neat, cm^{-1}): 1720 (C=O), 1604, 1521, 1434, 1271, 1190, 1112, 995; λ_{abs}(CH_2Cl_2)/nm: 419, 552, 597; HRMS-FAB calcd for $C_{62}H_{59}N_5O_6Zn$ ([M^+]): 10333756, found 1033.3792.

5,10,15-tris(4-methoxycarbonylphenyl)20-(4-N,N-didodecylaniline)porphyrinato zinc(II) (Zn1ND3E). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.15 (d, J = 4.7 Hz, 2H, β-py), 8.89-8.86 (m, 6H, β-py), 8.37-8.33 (m, 6H, Ar-H), 8.30-8.27 (m, 6H, Ar-H), 8.03 (d, J = 8.4 Hz, 2H, Ar-H), 7.01 (d, J = 8.6 Hz, 2H, Ar-H), 4.03 (s, 6H, COOMe), 4.01 (s, 3H, COOMe), 3.51 (t, J = 7.3 Hz, 4H, CH_2), 1.83 (p, J = 6.7 Hz, 4H, CH_2), 1.45-1.27 (m, 36H, CH_2), 0.87 (t, J = 7.7 Hz, 6H, CH_3); IR (Neat, cm^{-1}): 1720 (C=O), 1703 (C=O), 1602, 1519, 1434, 1269, 1190, 1112, 1101, 995, 819, 792, 761, 732, 715; λ_{abs}/nm (CH_2Cl_2): 418, 552, 598 HRMS-FAB calcd for $C_{74}H_{83}N_5O_6Zn$ ([M^+]): 1201.5635, found 1201.5676

5,10,15-tris(4-carbonylphenyl)20-(4-methylphenyl)porphyrinato zinc(II) (Zn1T3A). mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO-D_6) δ = 12.90 (s, 3H, COOH), 8.82 (d, J = 4.7 Hz, 2H, β-py), 8.77 (s, 4H, β-py), 8.75 (d, J = 4.7 Hz, 2H, β-py), 8.34 (d, J = 8.1 Hz, 6H, Ar-H), 8.24 (d, J = 8.0 Hz, 6H, Ar-H), 8.01 (d, J = 7.8 Hz, 2H, Ar-H), 7.52 (d, J = 7.8 Hz, 2H, Ar-H), 2.65 (s, 3H, Me); IR (Neat, cm^{-1}): 1682 (C=O), 1602, 1404, 1266, 1230, 1179, 1100, 1072, 995, 794, 766, 717; λ_{abs}/nm (THF), (ε/10^3 M^{-1} cm^{-1}): 424 (357), 557 (15) 599 (6); λ_{em}/nm (THF): 606, 652; HRMS-FAB calcd for $C_{48}H_{30}N_4O_6Zn$ ([M^+]): 822.1457, found 822.1464.

5,10,15-tris(4-carbonylphenyl)20-(undecyl)porphyrinato zinc(II) (Zn1U3A). mp > 300 °C; ^{1}H NMR (300 MHz, DMSO-D_6) δ = 13.24 (s, 3H, COOH), 9.69 (d, J = 4.5 Hz, 2H, β-py), 8.81 (d, J

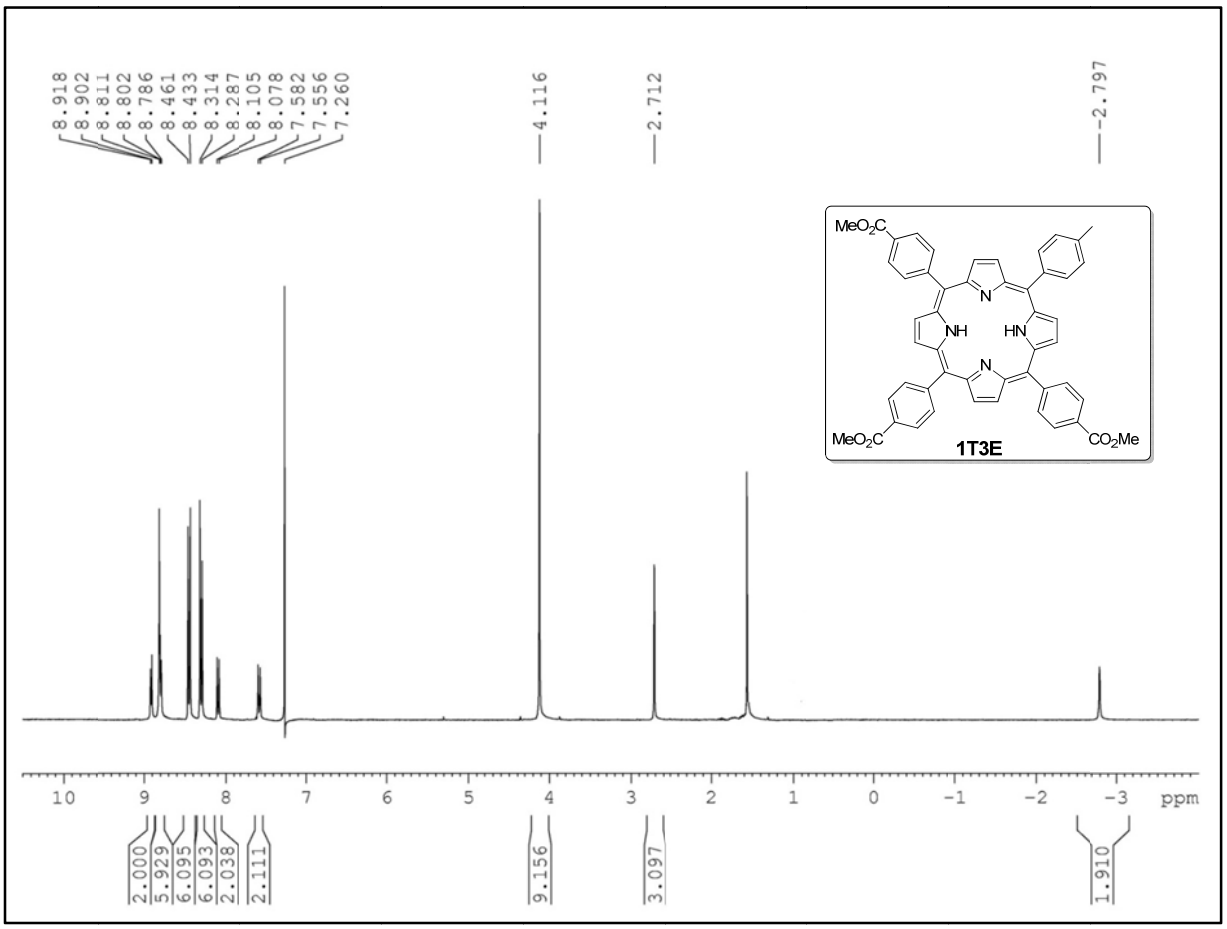
= 4.4 Hz, 2H, β-py), 8.72 (s, 4H, β-py), 8.37- 8.33 (m, 6H, Ar-H), 8.29-8.25 (m, 6H, Ar-H), 5.06 (t, J = 7.2, 2H, CH_2),1.49 (p, J = 6.1 Hz, 2H, CH_2) 1.49 (p, J = 6.1 Hz, 2H, CH_2), 1.33-1.09 (m, 14 H, CH_2), 0.82 (t, J = 6.8 Hz, 3H, CH_3); IR (Neat, cm^{-1}): 1685 (C=O), 1604, 1421, 1314, 1219, 998, 792, 760, 714; λ_{abs}/nm (THF), ($\varepsilon/10^3$ M^{-1} cm^{-1}): 425 (474), 559 (20), 601 (9); λ_{em}/nm (THF): 606, 652; HRMS-FAB calcd for $C_{52}H_{46}N_4O_6Zn$ ($[M^+]$): 886.2709, found 886.2709.

5,10,15-tris(4-carbonylphenyl)20-(4-diphenylaminophenyl)porphyrinato zinc(II) (Zn1TPA3A). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$+DMSO-D_6) δ =12.90 (s, 3H, COOH), 8.96 (d, J = 4.5 Hz, 2H, β-py), 8.79-8.76 (m, 6H, β-py), 8.35-8,32 (m, 6H, Ar-H), 8.25-8.21 (m, 6H, Ar-H), 8.00-7.99 (m, 2H, Ar-H), 7.39-7.32 (m, 10H, Ar-H), 7.10-7.06 (m, 2H, Ar-H); IR (Neat, cm^{-1}): 1686 (C=O), 1605, 1484, 1406, 1313, 1274, 1230, 1190, 1177, 996, 867; λ_{abs}/nm (THF), ($\varepsilon/10^3$ M^{-1} cm^{-1}): 427 (318), 558 (21), 659 (12); λ_{em}/nm (THF): 611; HRMS-FAB calcd for $C_{62}H_{37}N_5O_6Zn$ ($[M^+]$): 975.2035, found 975.2037.

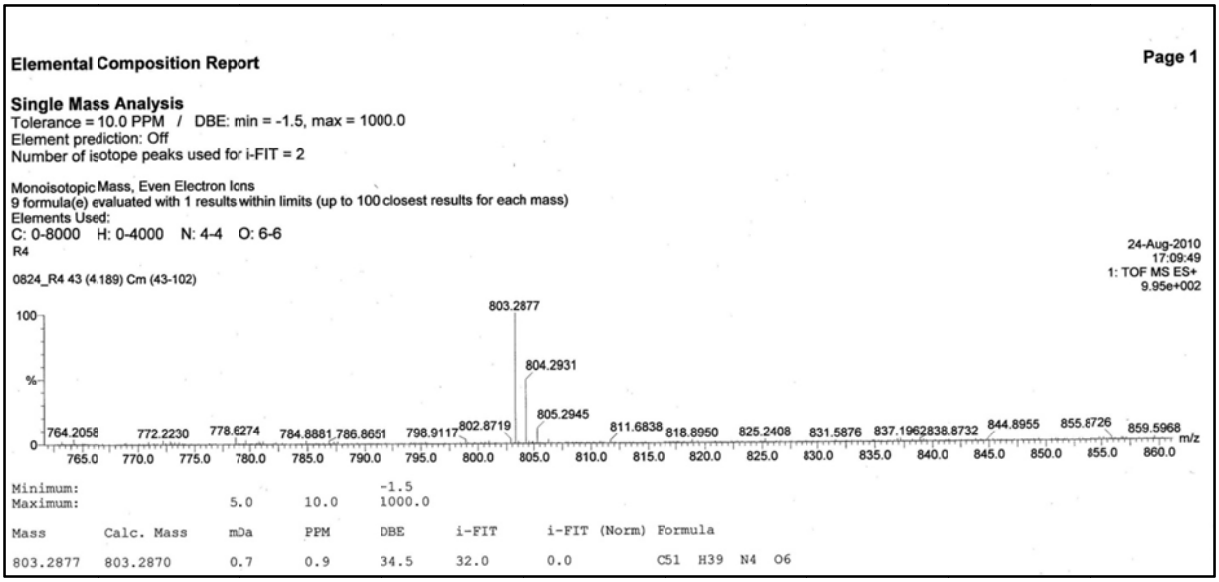
5,10,15-tris(4-carbonylphenyl)20-(4-N,N-dihexylaniline)porphyrinato zinc(II) (Zn1NH3A). mp > 300 °C; ^{1}H NMR (400 MHz, DMSO-D_6) δ = 13.47 (s, 3H, COOH), 8.94 (d, J = 4.6 Hz, 2H, β-py), 8.77-8.75 (m, 6H, β-py), 8.37 (d, J = 7.9 Hz, 6H, Ar-H), 8.30 (d, J = 7.8 Hz, 6H, Ar-H), 7.95 (d, J = 8.4 Hz, 2H, Ar-H), 7.01 (d, J = 8.3 Hz, 2H, Ar-H), 3.48 (t, J = 6.5 Hz, 4H, CH_2), 1.73 (p, J = 6.2 Hz, 4H, CH_2), 1.37-1.36 (m, 12H, CH_2), 0.91 (t, J = 6.9 Hz, 6H, CH_3); IR (Neat, cm^{-1}): 1683 (C=O), 1602, 15543, 1402, 1338, 1274, 1204, 995, 867, 794, 765, 717; λ_{abs}/nm (THF), ($\varepsilon/10^3$ M^{-1} cm^{-1}): 425 (178), 559 (13), 603 (8); λ_{em}/nm (THF): 622; HRMS-FAB calcd for $C_{59}H_{53}N_5O_6Zn$ ($[M+H]^+$) 9923365, found 992.3388.

5,10,15-tris(4-carbonylphenyl)20-(4-N,N-didodecylaniline)porphyrinato zinc(II) (Zn1ND3A). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$+DMSO-D_6) δ = δ = 8.97 (d, J = 4.5 Hz, 2H, β-py), 8.76-8.74 (m, 6H, β-py), 8.34 (d, J = 7.8 Hz, 6H, Ar-H), 8.23 (d, J = 7.9 Hz, 6H, Ar-H), 7.93 (d, J = 8.6 Hz, 2H, Ar-H), 6.95 (d, J = 8.5 Hz, 2H, Ar-H), 3.47 (t, J = 6.6 Hz, 4H, CH_2), 1.77 (m, 4H, CH_2), 1.36-1.21 (m, 36H, CH_2), 0.81 (t, J = 6.1 Hz, 6H, CH_3); IR (Neat, cm^{-1}): 1687 (C=O), 1604, 1519, 1402, 1274, 1261, 1202, 1118, 1024, 993, 794, 765, 717; λ_{abs}/nm (THF), ($\varepsilon/10^3$ M^{-1} cm^{-1}): 425 (143), 560 (12), 603 (8); λ_{em}/nm (THF): 624; HRMS-FAB calcd for $C_{71}H_{77}N_5O_6Zn$ ([M+H]): 1160.5243, found 1160.5288.

NMR spectrum of 1T3E



HR-MS of 1T3E



Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 100 closest results for each mass)
Elements Used:
C: 0-8000 H: 0-4000 N: 4-4 O: 6-6
R4

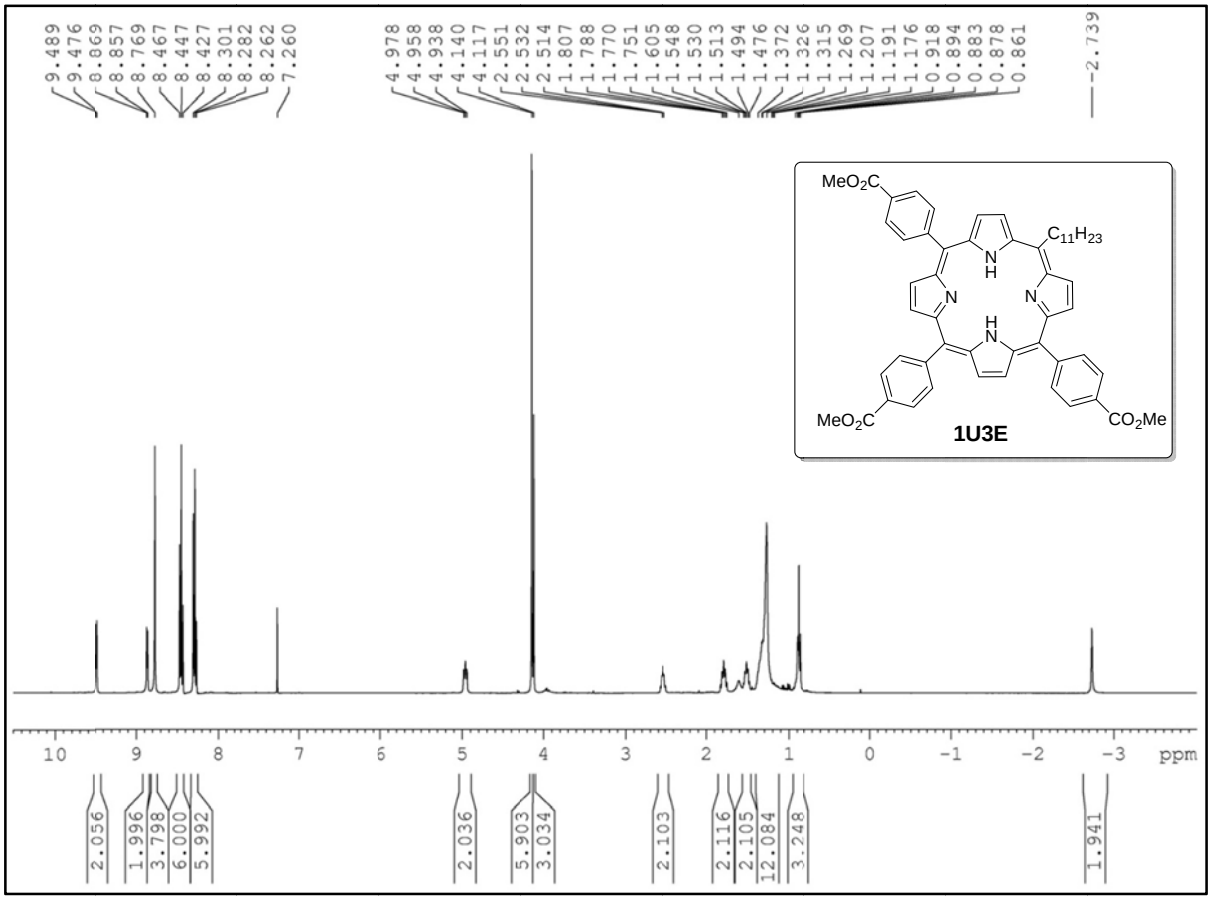
24-Aug-2010
17:09:49
1: TOF MS ES+
9.95e+002

0824_R4 43 (4.189) Cm (43-102)

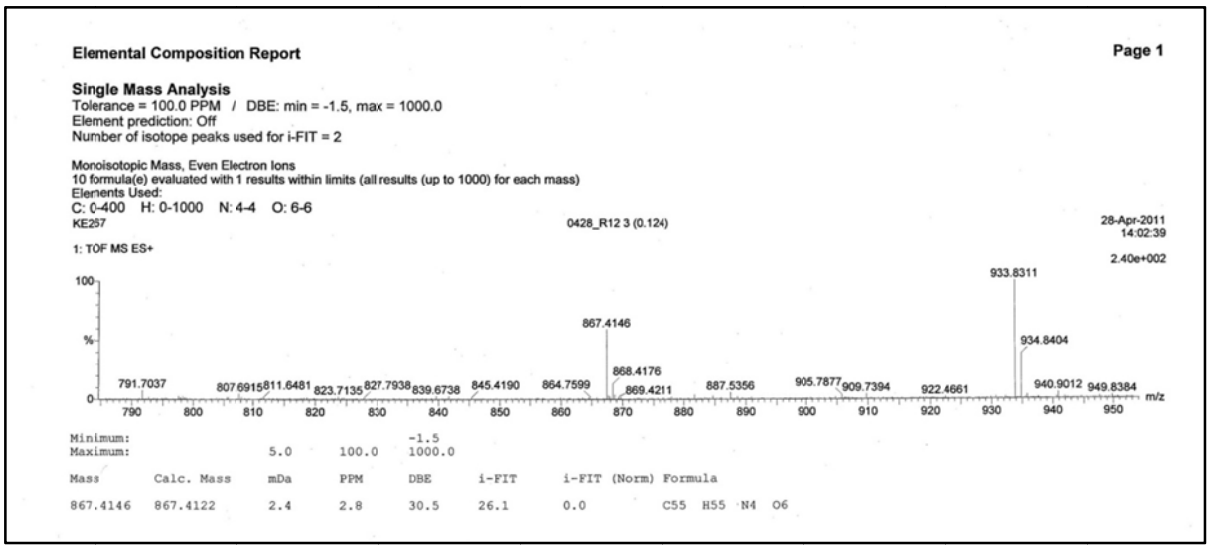
803.2877
804.2931
805.2945
764.2058
772.2230
778.6274
784.8881
786.8651
798.9117
802.8719
811.6838
818.8950
825.2408
831.5876
837.1962
838.8732
844.8955
855.8726
859.5968
m/z

Minimum:				-1.5			
Maximum:		5.0	10.0	1000.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
803.2877	803.2870	0.7	0.9	34.5	32.0	0.0	C51 H39 N4 O6

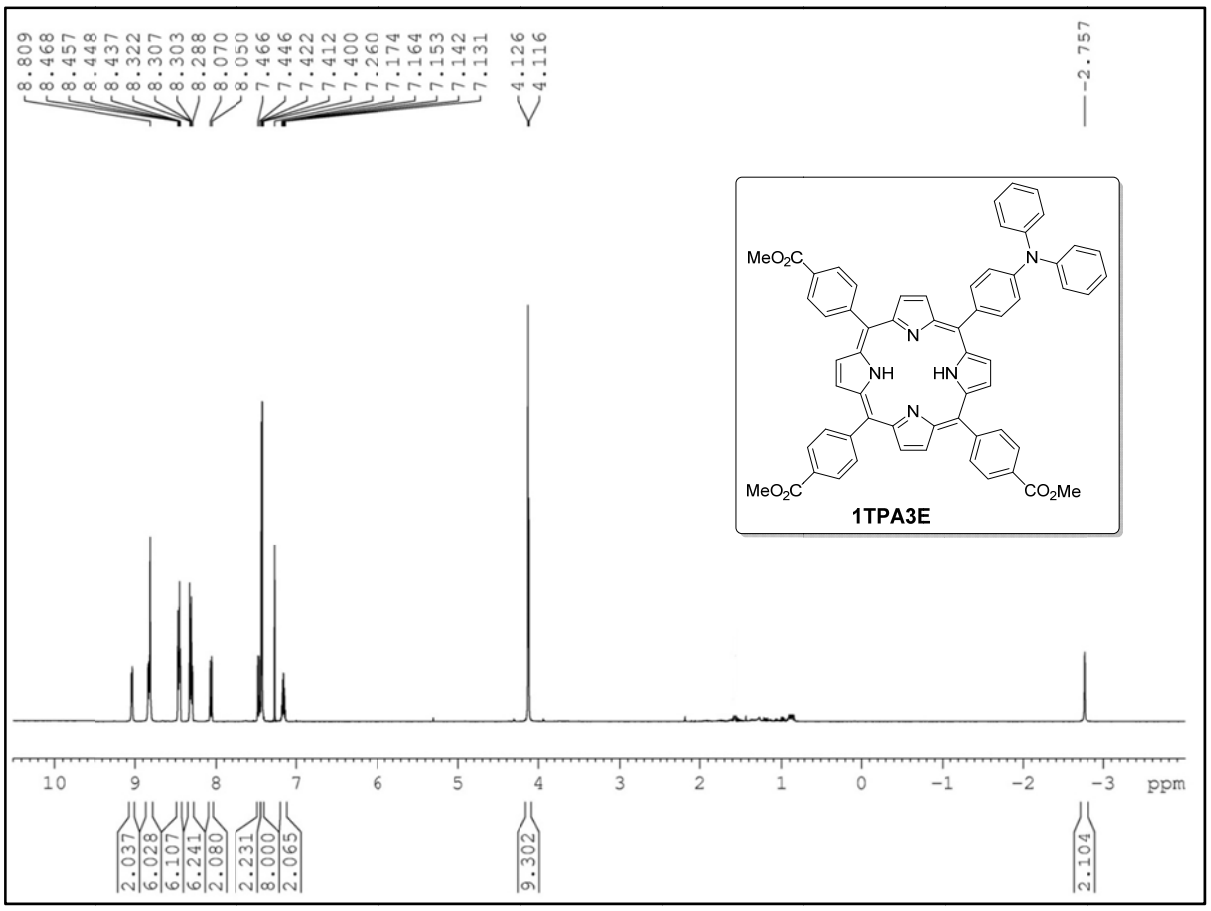
NMR Spectrum of 1U3E



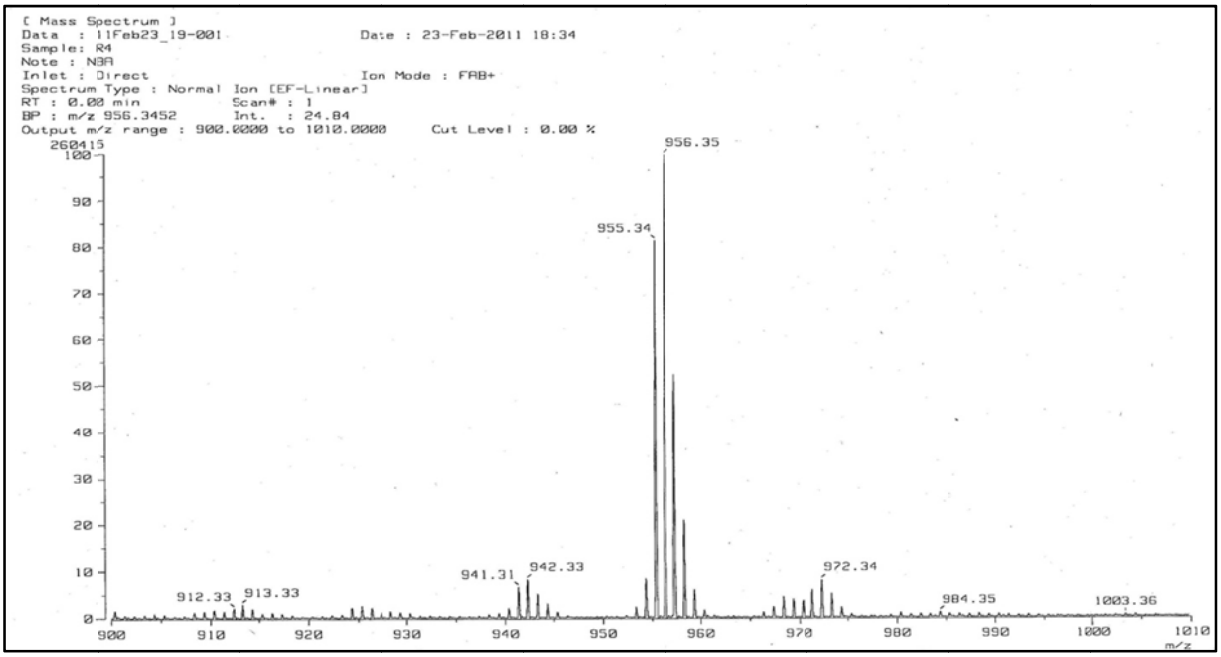
HR-MS of 1U3E



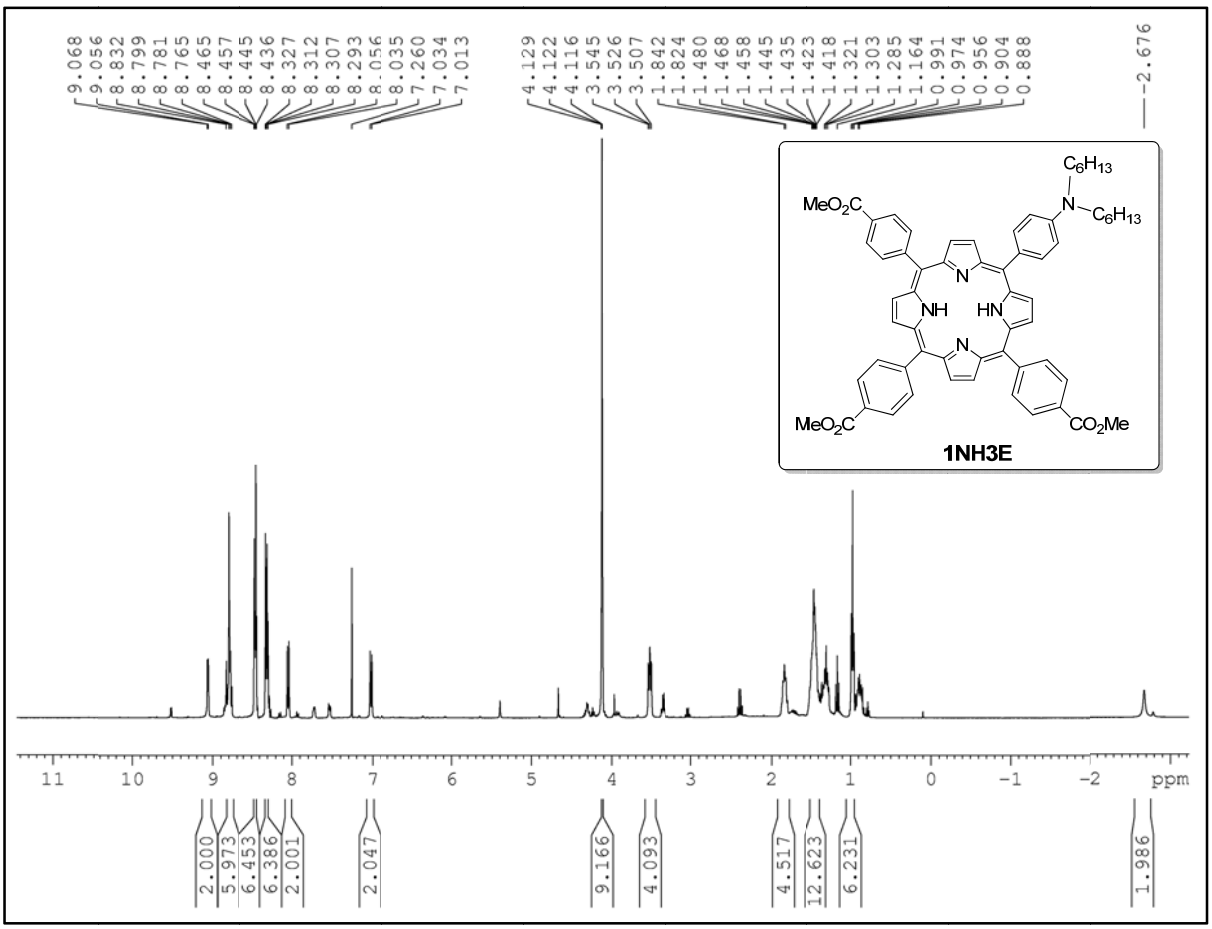
NMR Spectrum of 1TPA3E



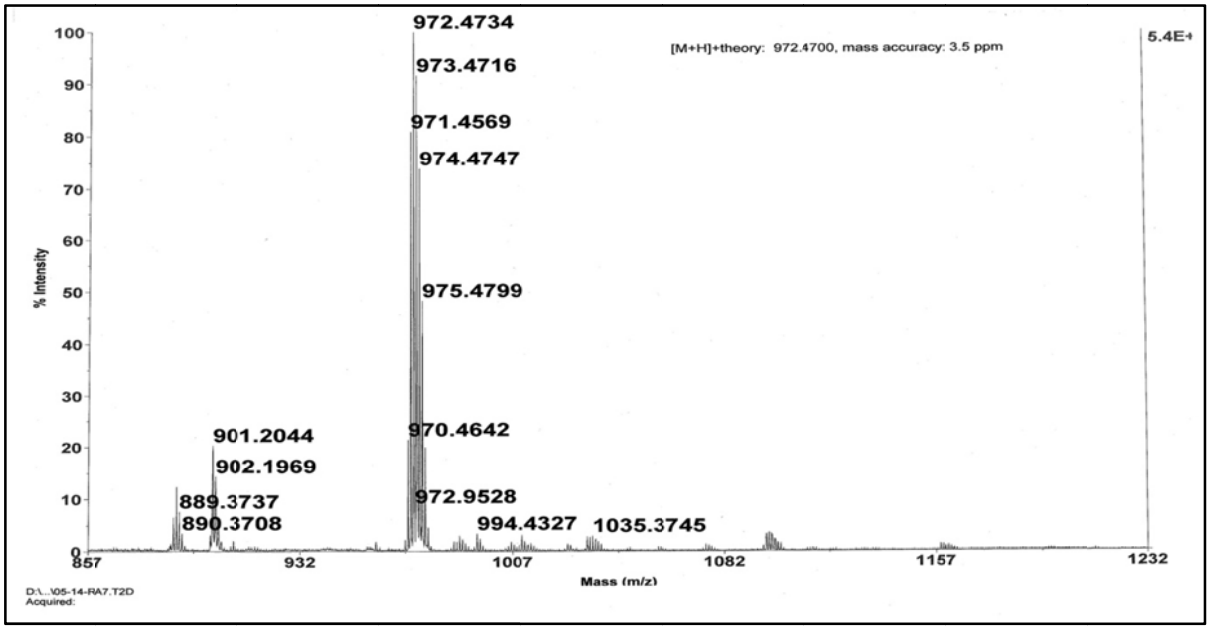
HR-MS of 1TPA3E



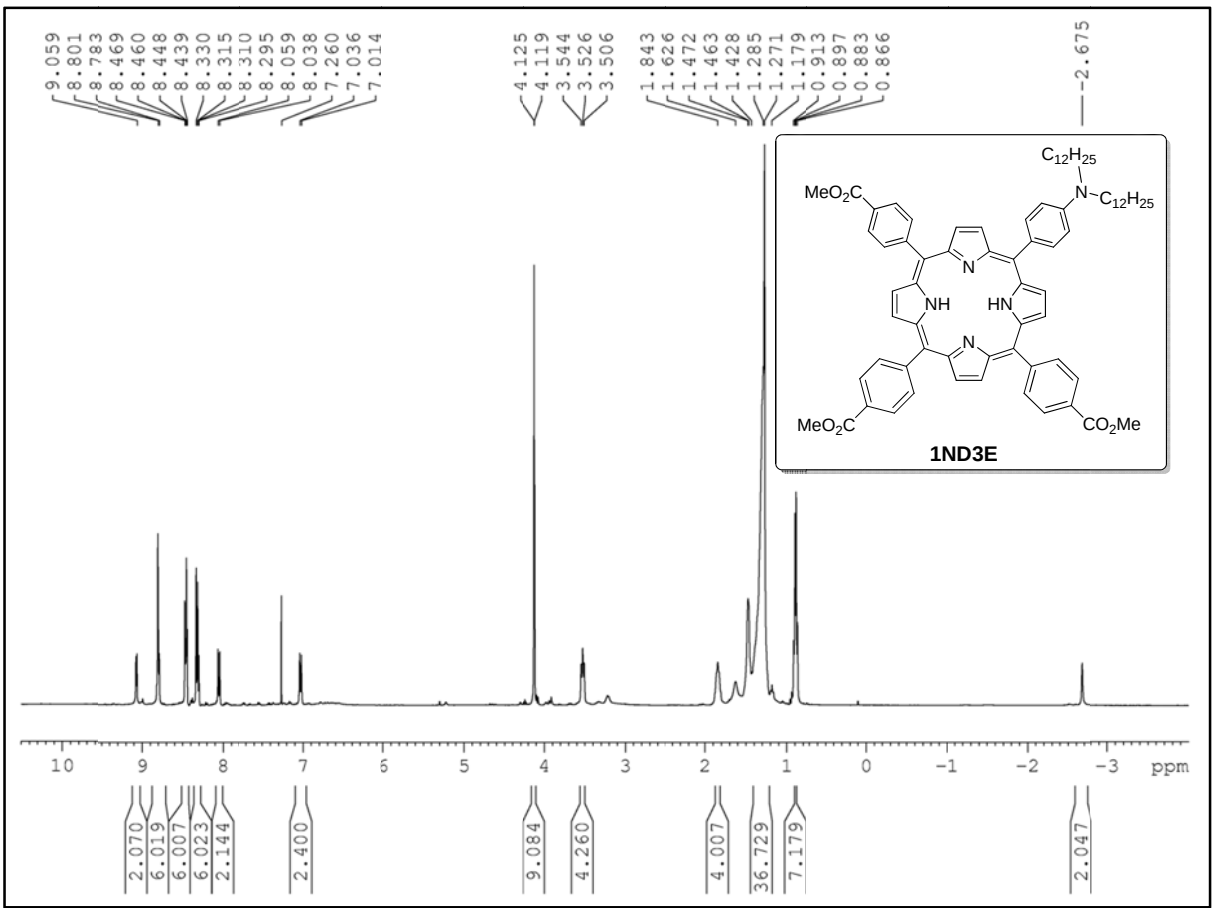
NMR Spectrum of 1NH3E



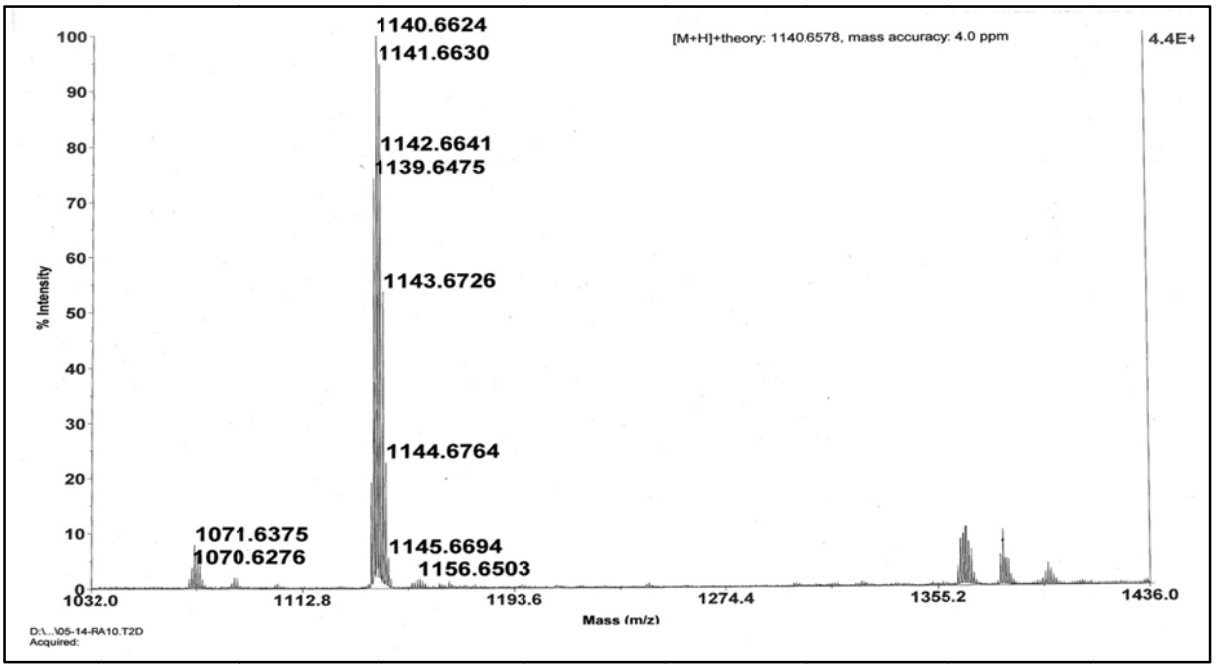
HR-MS of 1NH3E



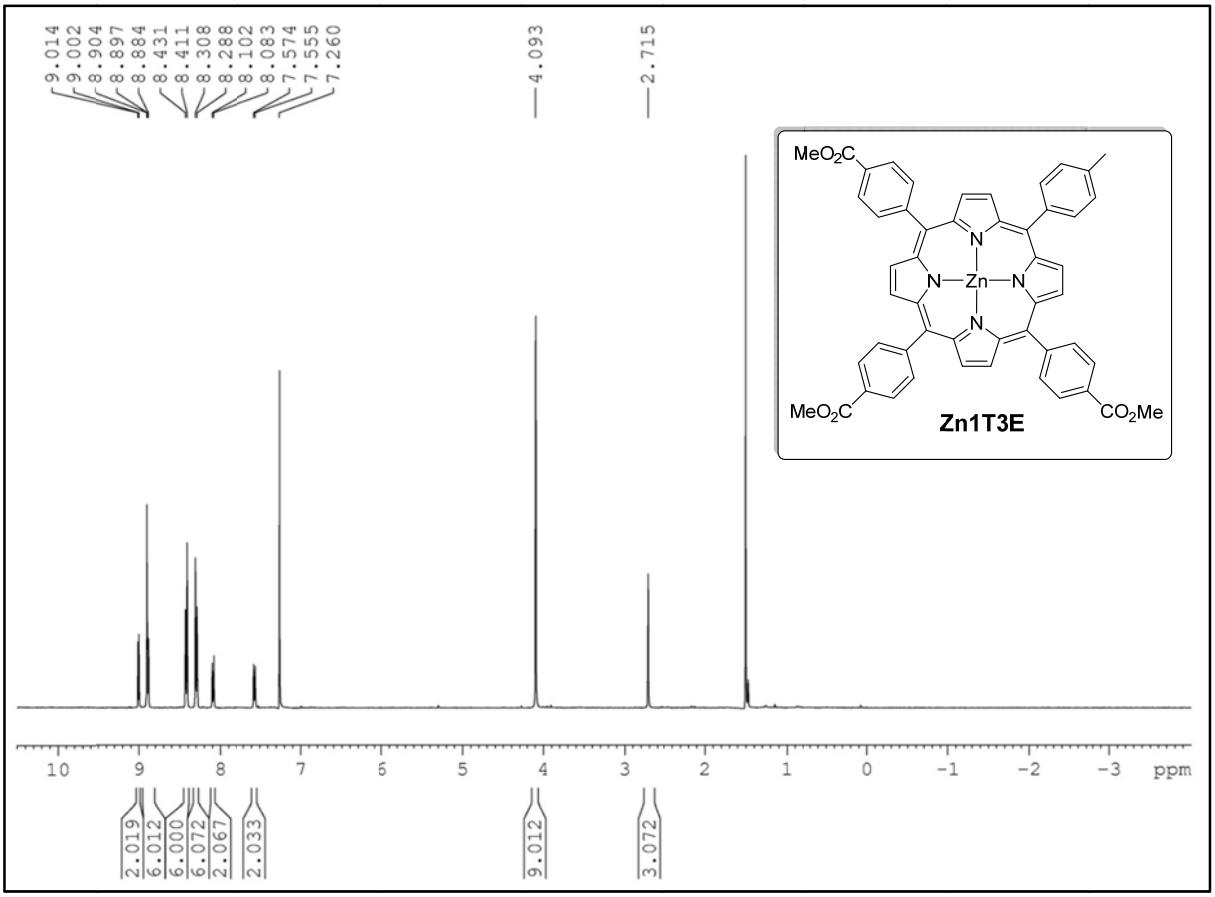
NMR Spectrum of 1ND3E



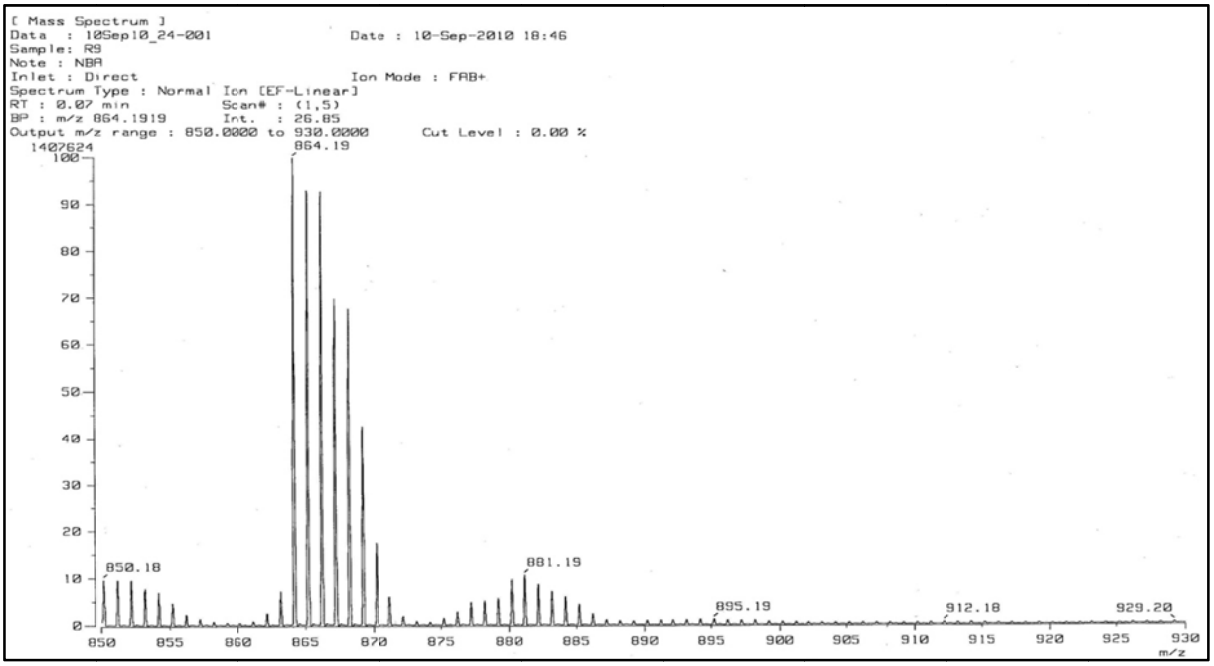
HR-MS of 1ND3E



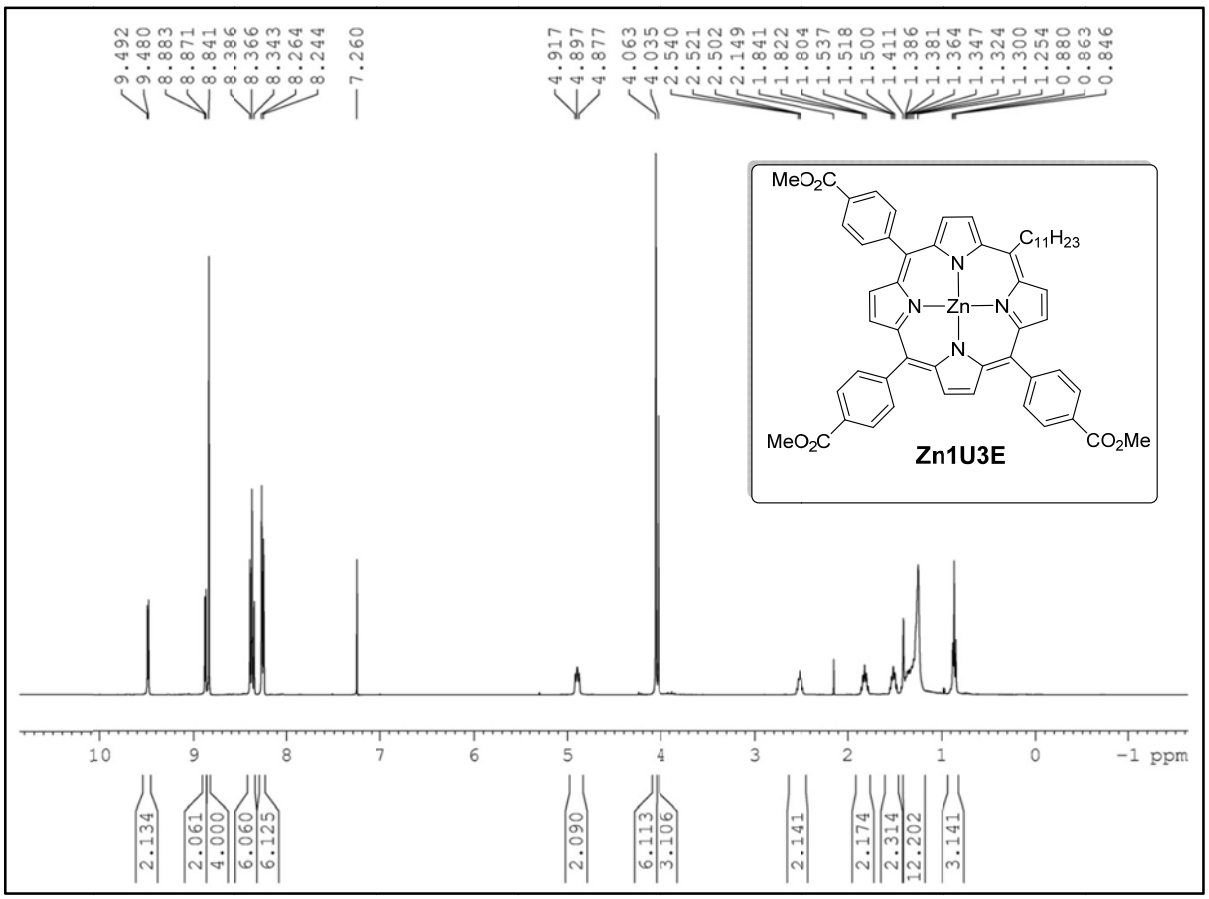
NMR Spectrum of Zn1T3E



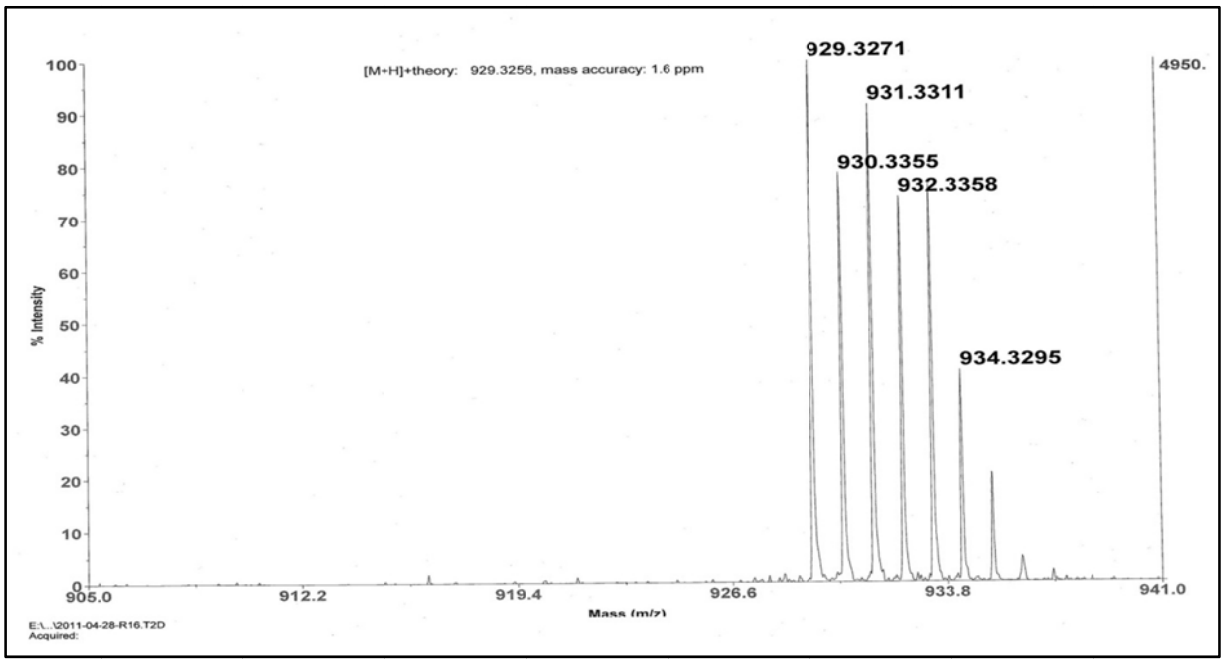
HR-MS of Zn1T3E



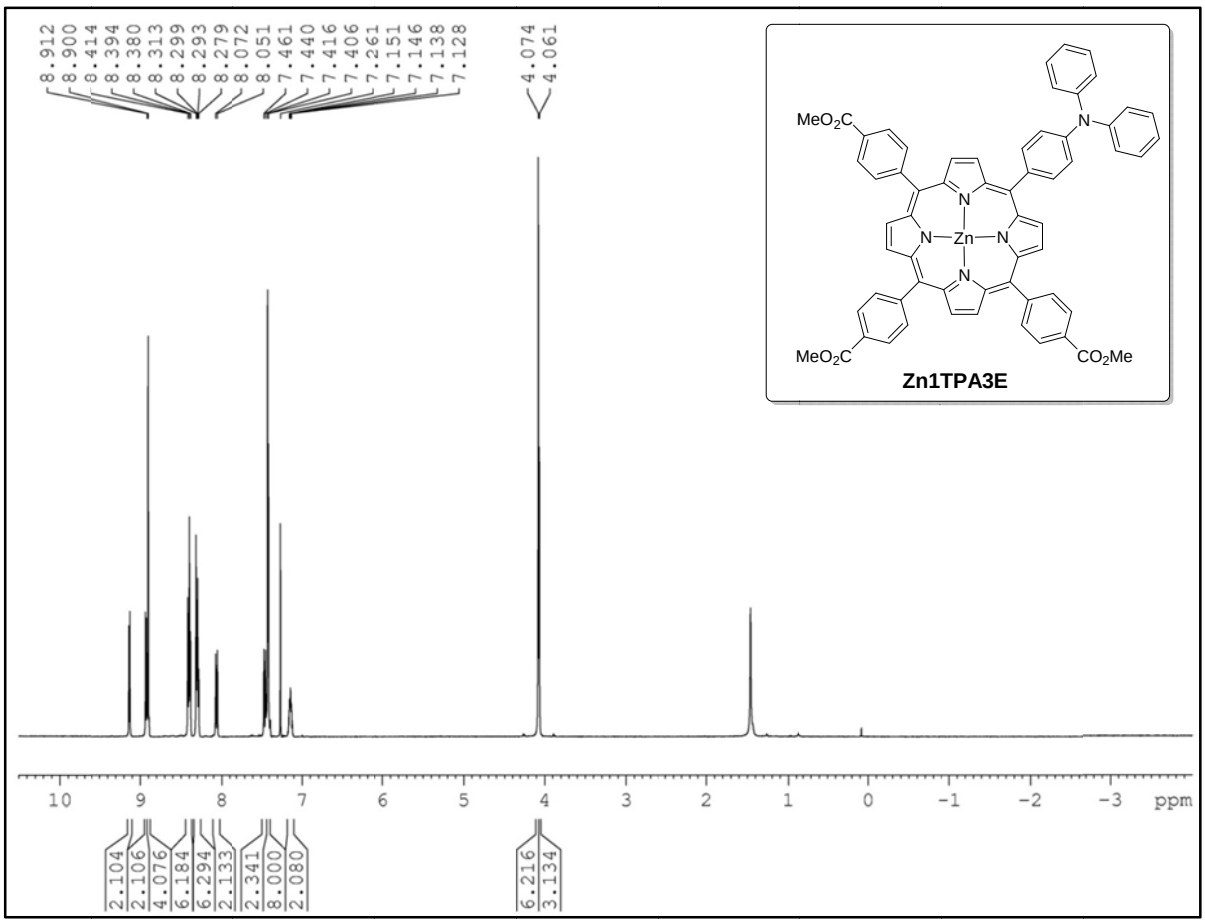
NMR Spectrum of Zn1U3E



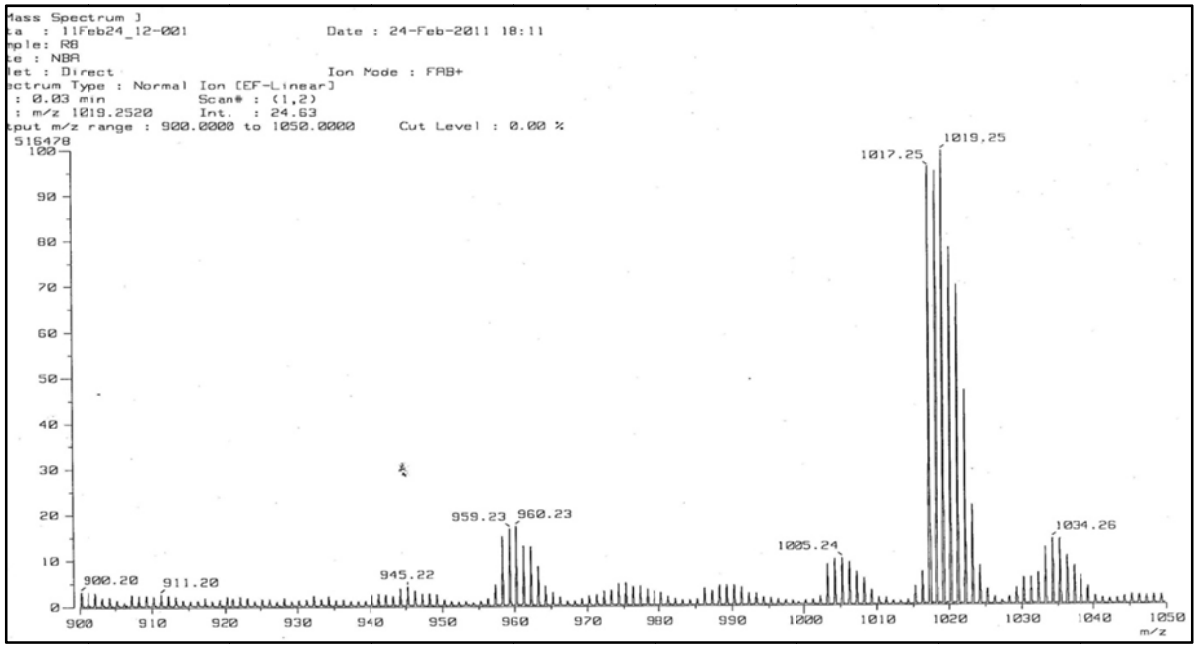
HR-MS of Zn1U3E



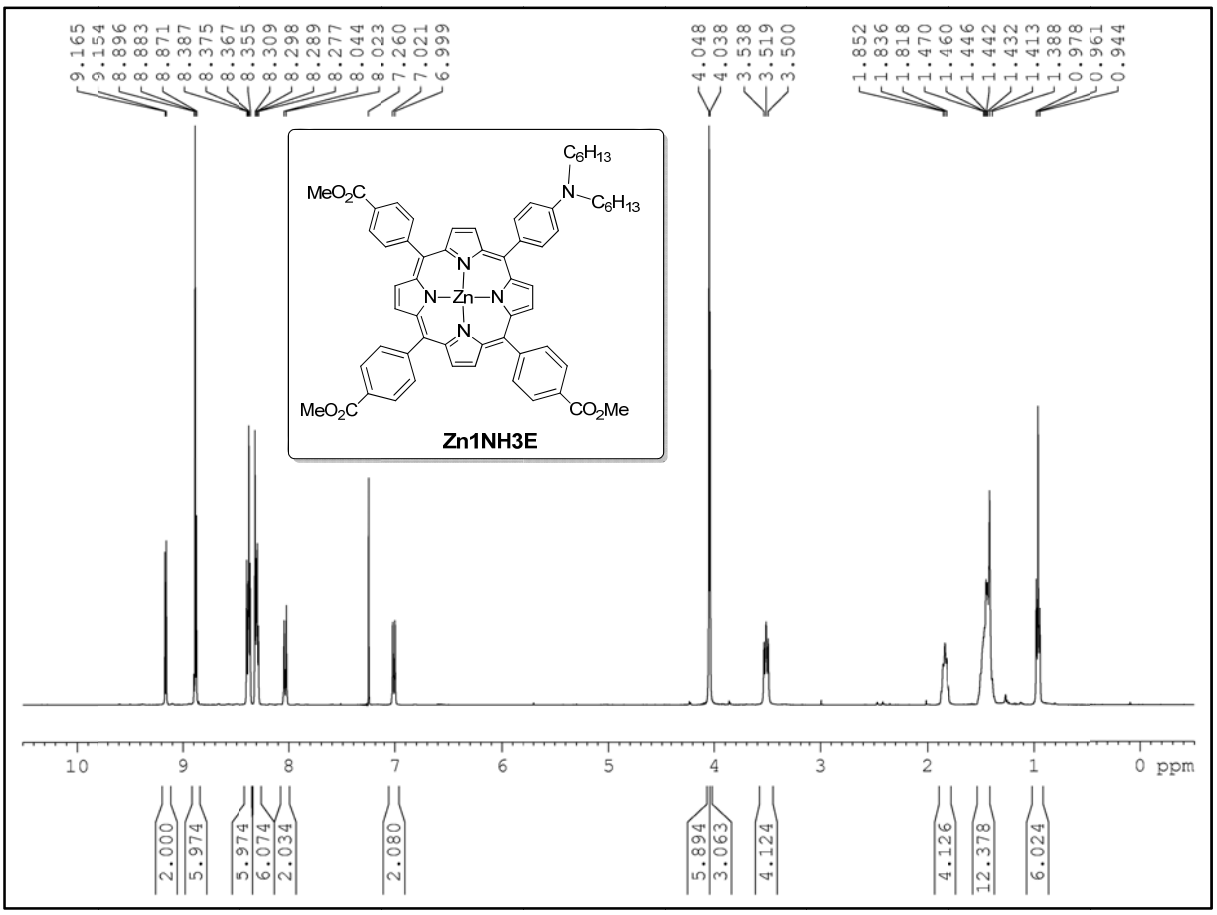
NMR Spectrum of Zn1TPA3E



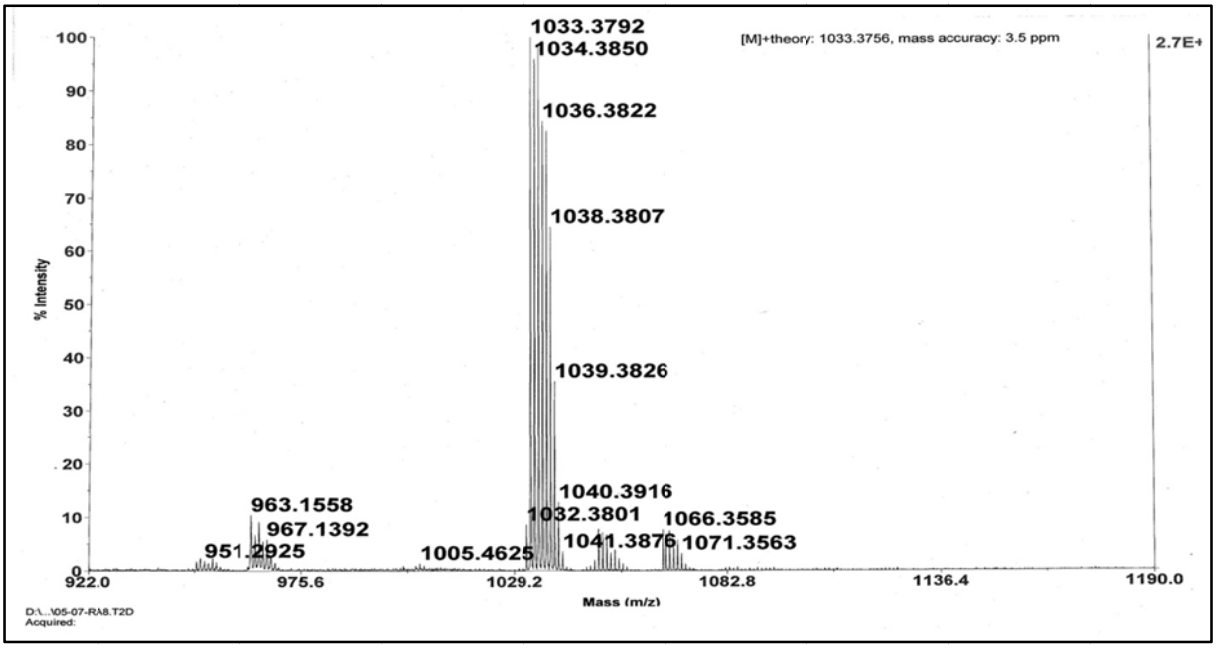
HR-MS of Zn1TPA3E



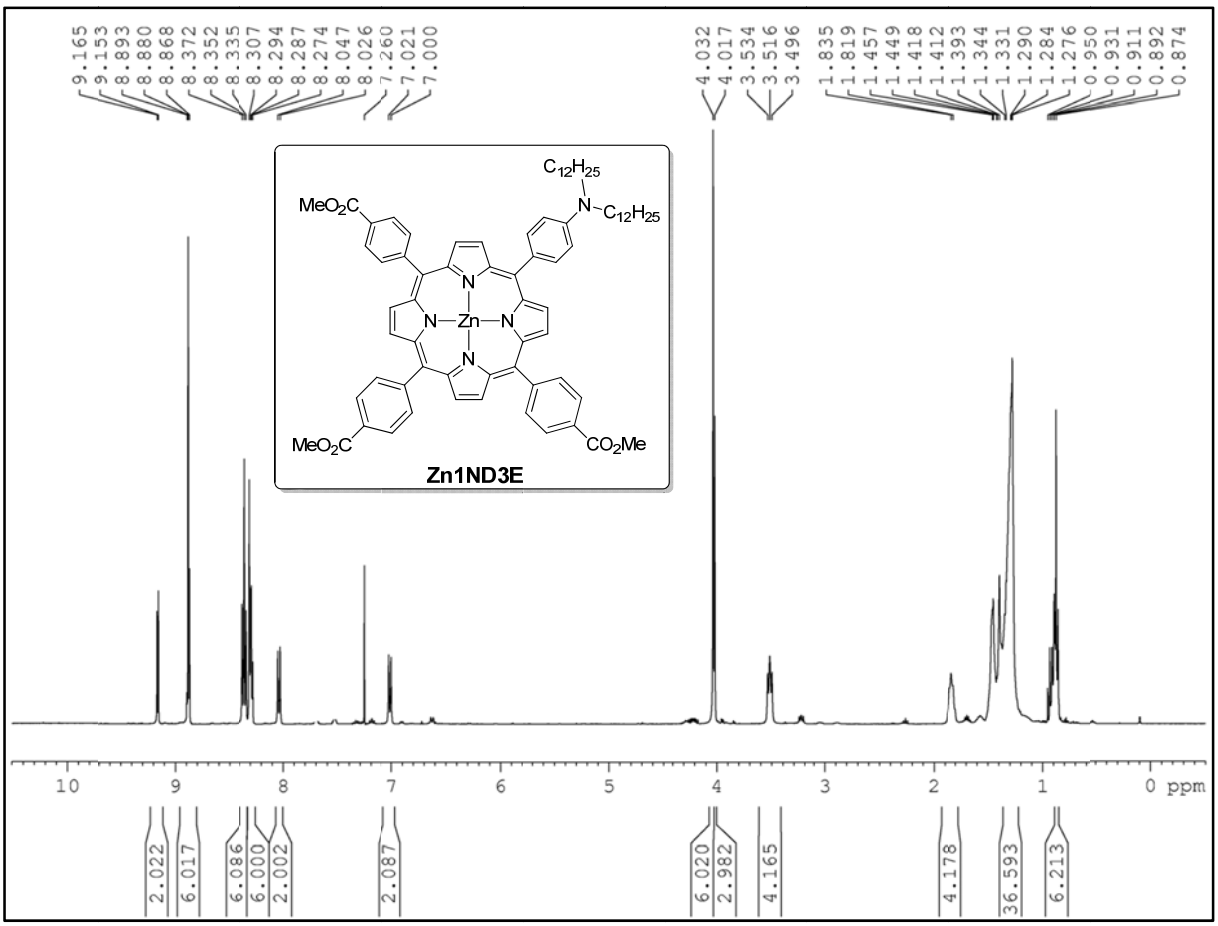
NMR Spectrum of Zn1NH3E



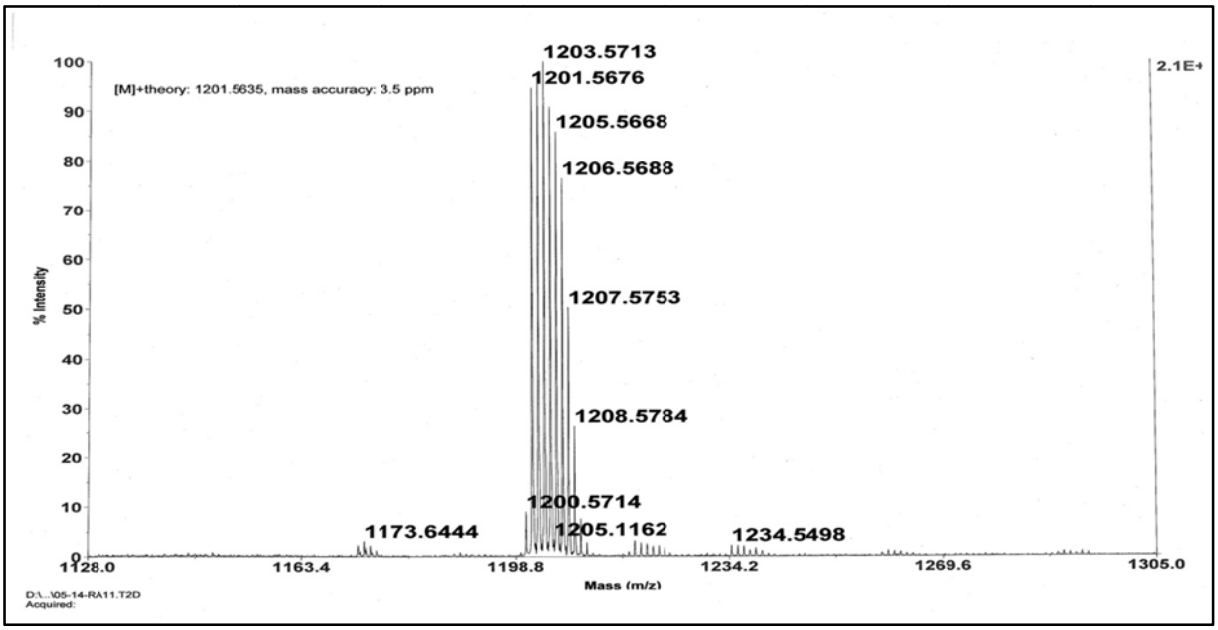
HR-MS of Zn1NH3E



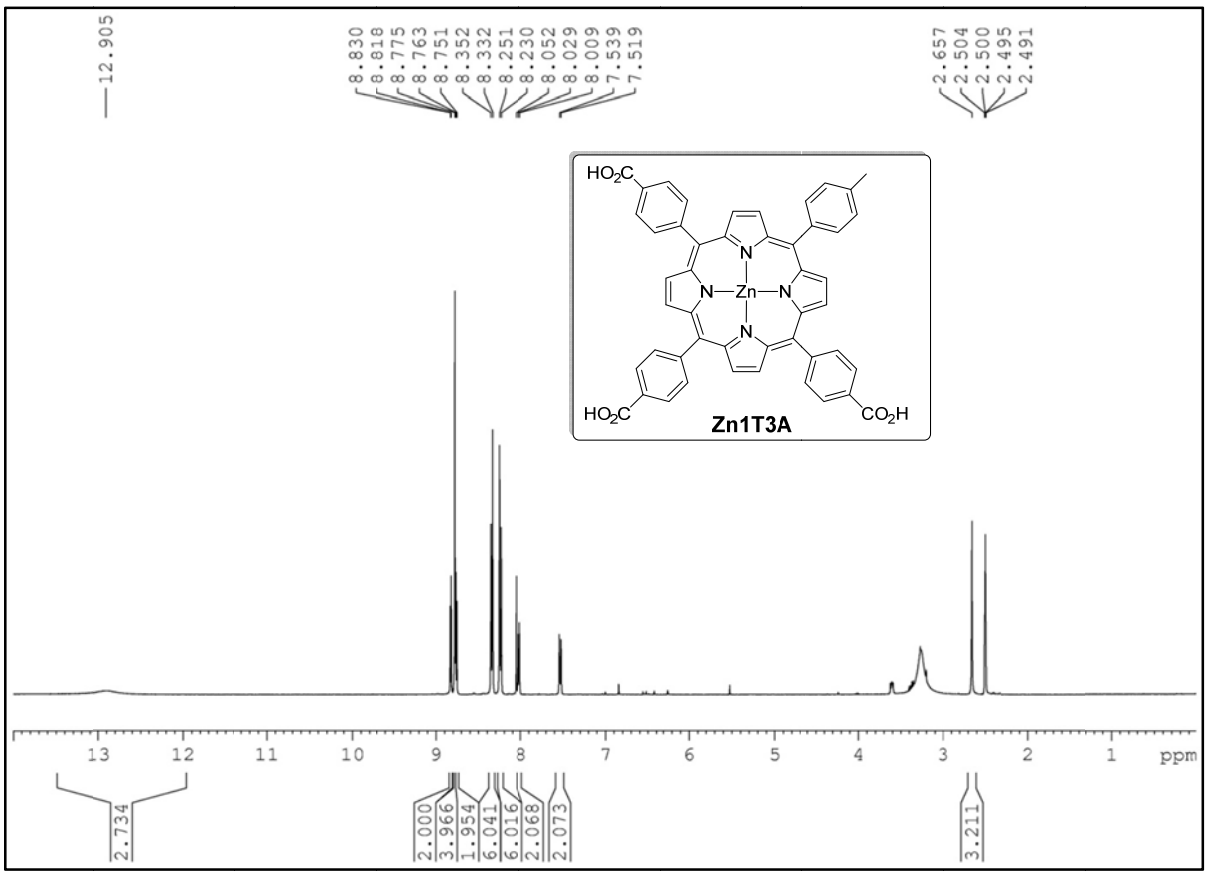
MR Spectrum of Zn1ND3E



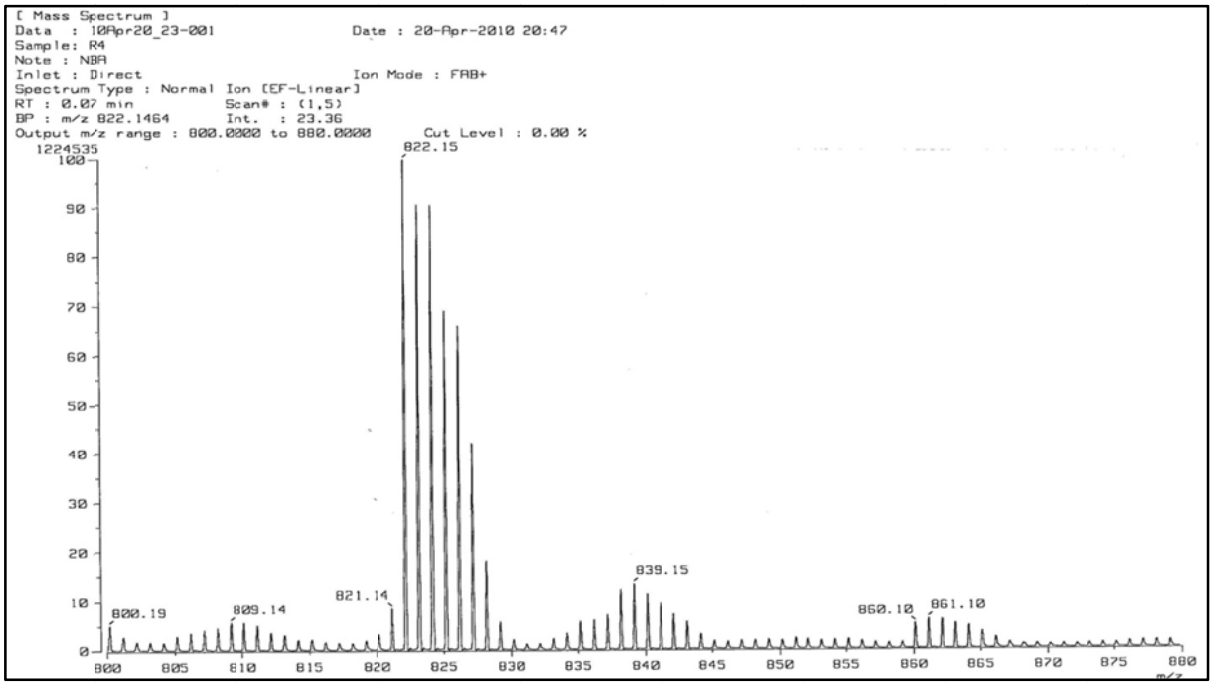
HR-MS of Zn1ND3E



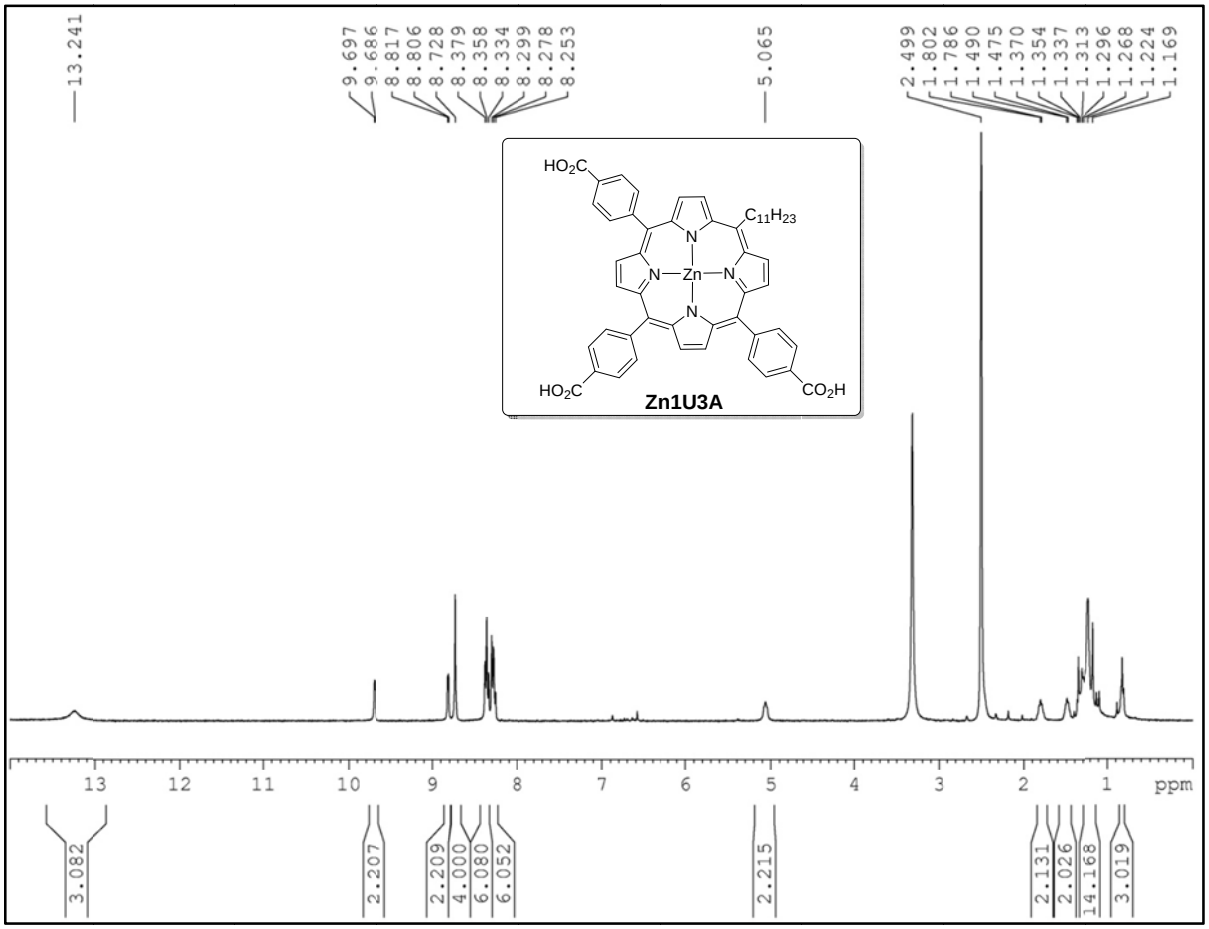
NMR Spectrum of Zn1T3A



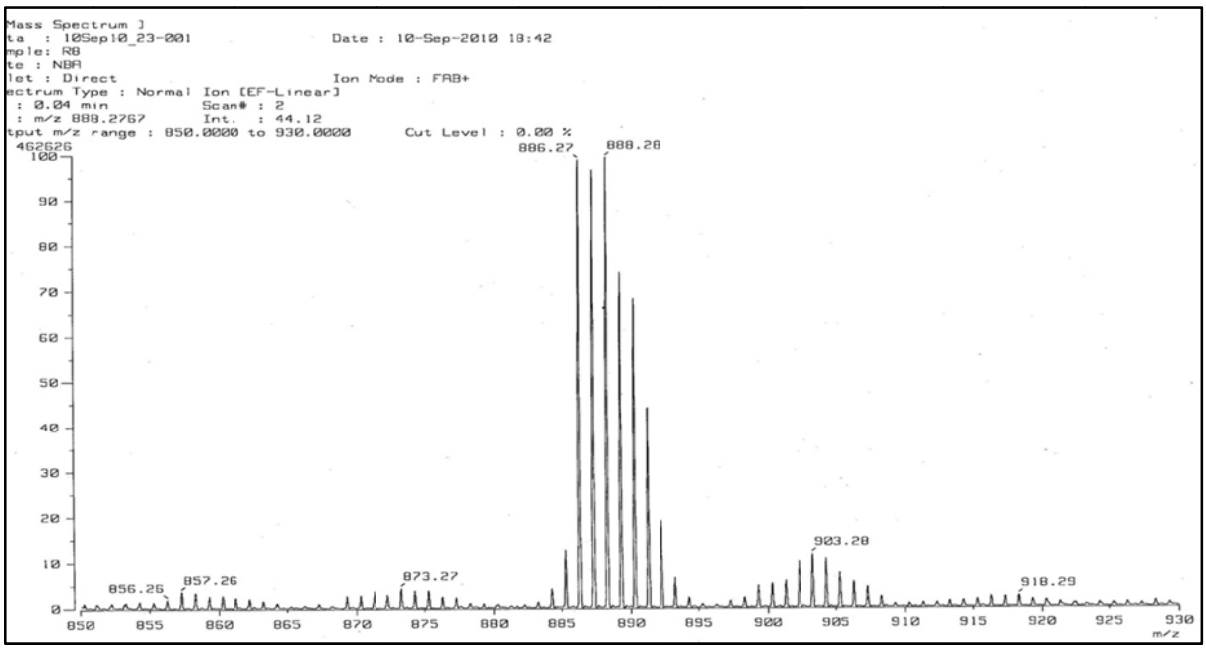
HR-MS of Zn1T3A



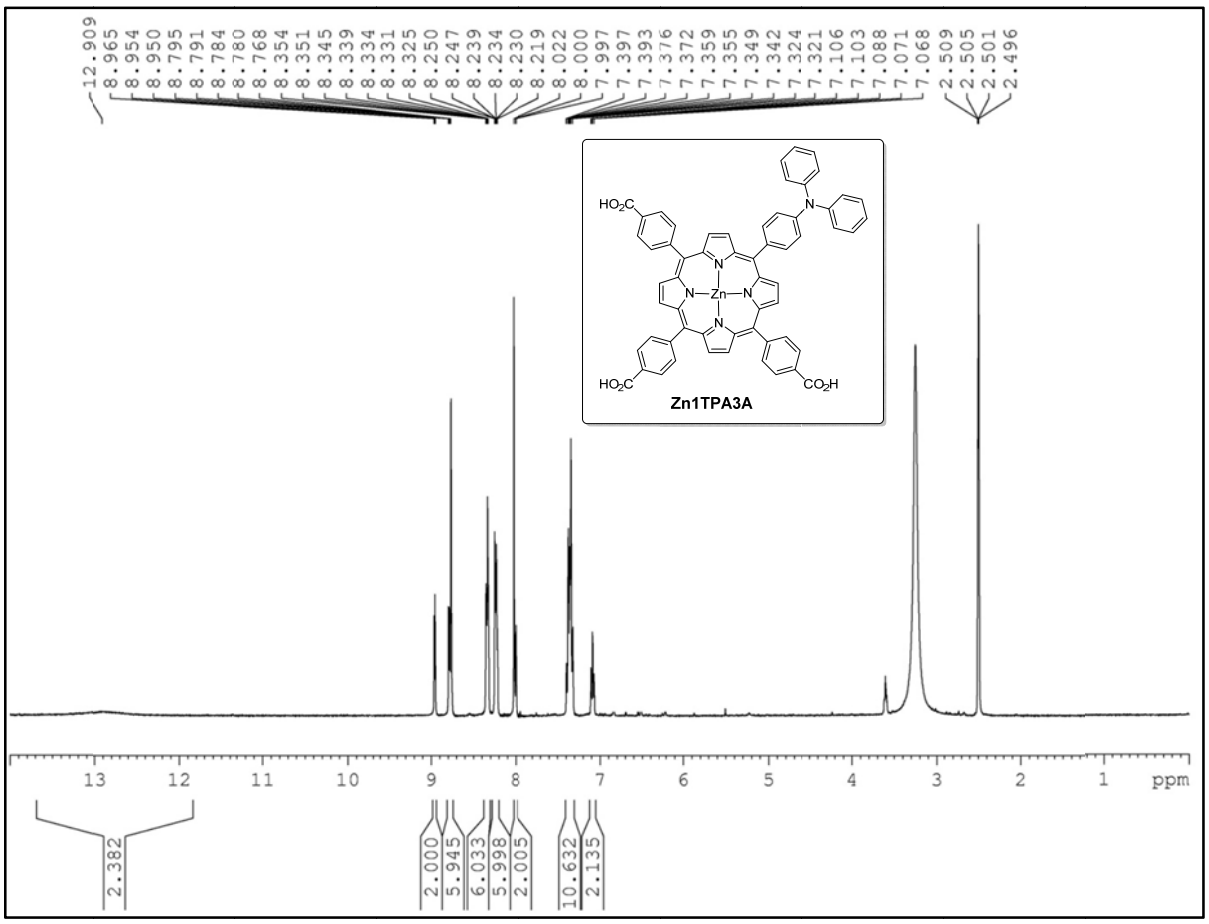
NMR Spectrum of Zn1U3A



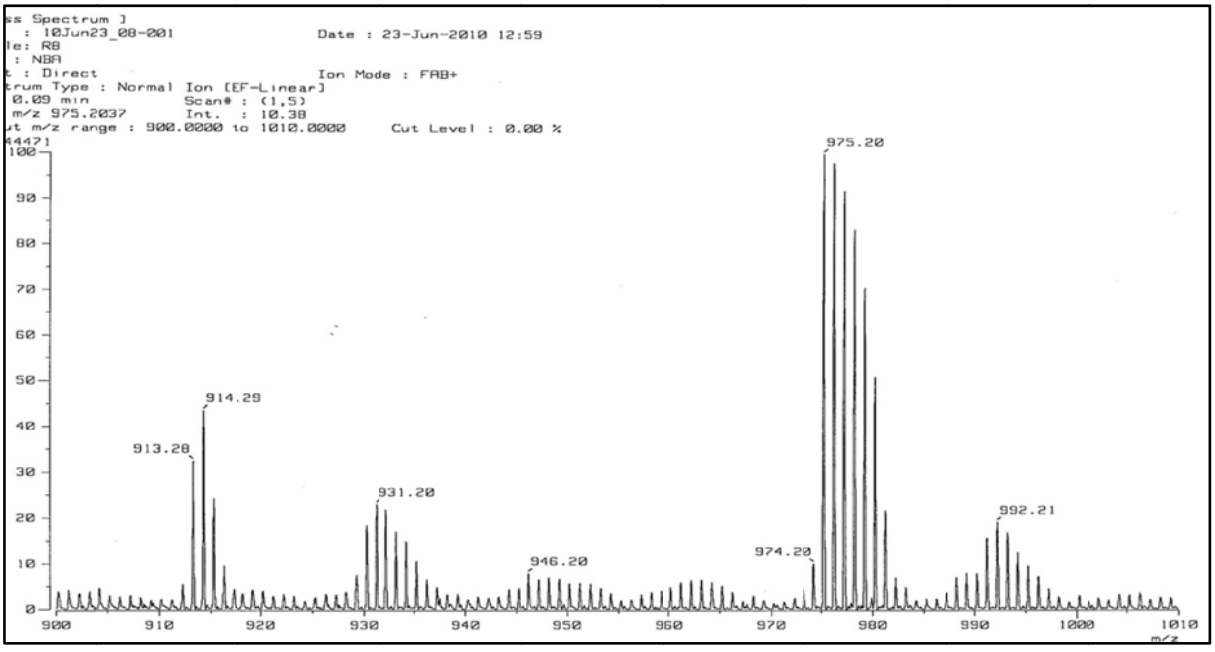
HR-MS of Zn1U3A



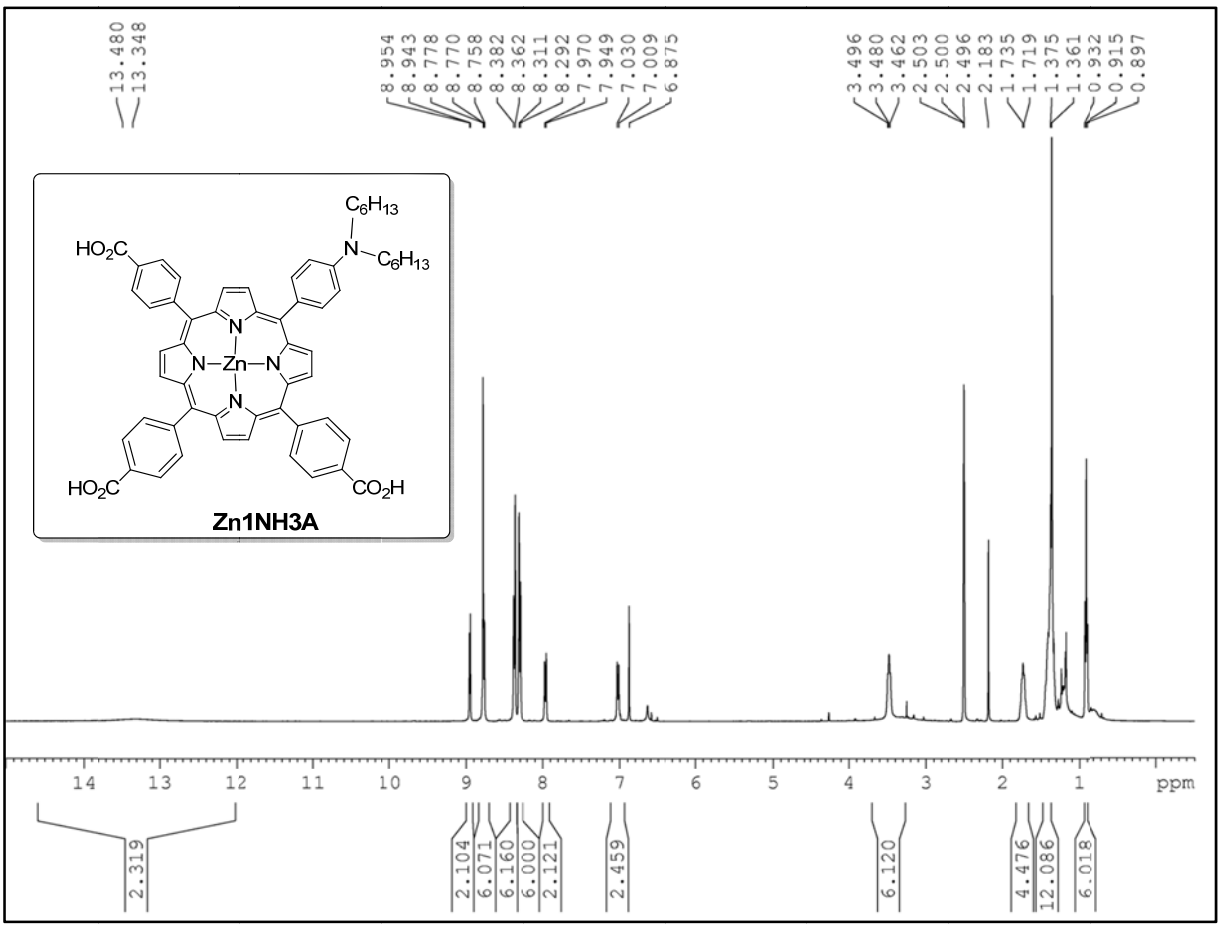
NMR Spectrum of Zn1TPA3A



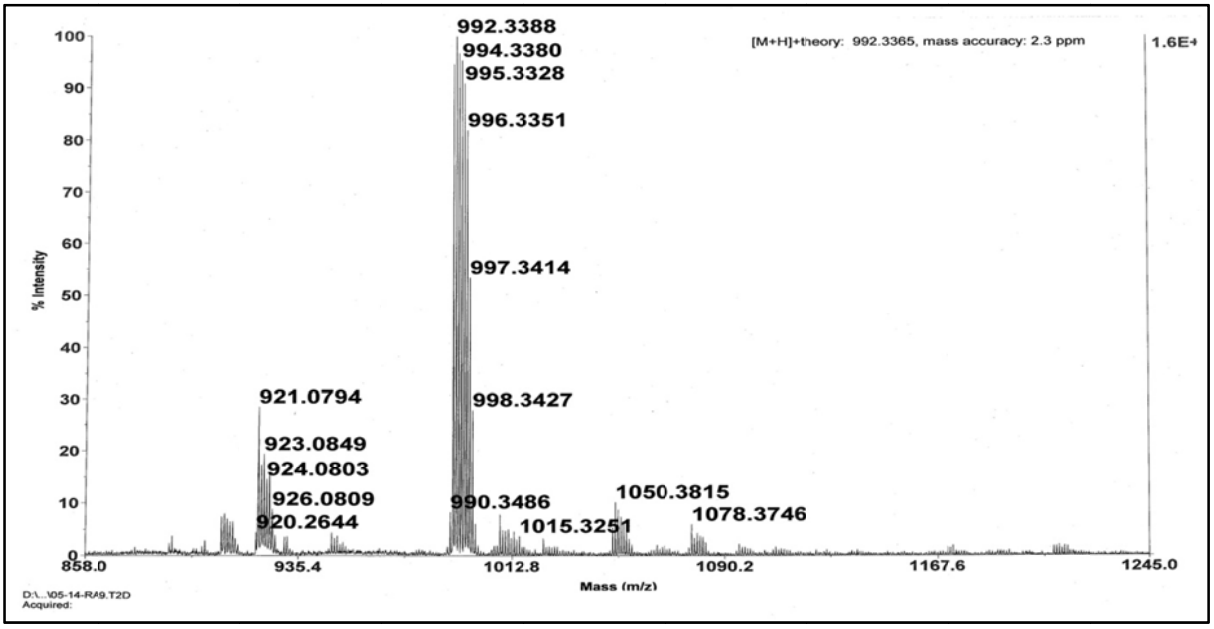
HR-MS of Zn1TPA3A



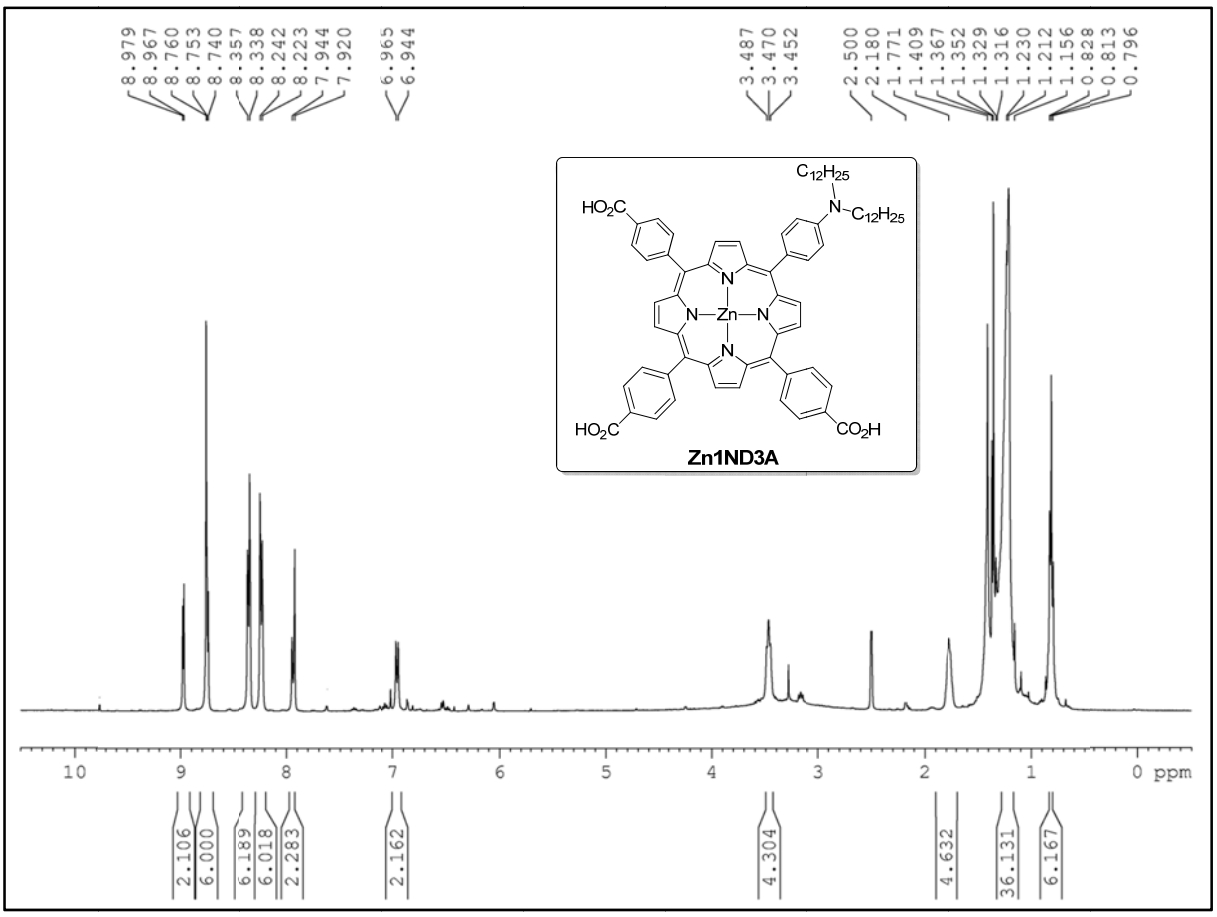
NMR Spectrum of Zn1NH3A



HR-MS of Zn1NH3A



NMR Spectrum of Zn1ND3A



HR-MS of Zn1ND3A