Supporting information

meso-Thiophenium porphyrins and their Zn(II) complexes: A new category of cationic photosensitizers.

Zeaul Hoque Mazumdar,[a]† Debdulal Sharma,[a]† Avinaba Mukherjee,[b] Samita Basu,[c] Pradeep Kumar Shukla,[d] and Tarun Jha[e] and Devashish Sengupta.[a]*

a. Department of Chemistry, Assam University, Silchar-788011, Assam, India.

b. Department of Zoology, Charuchandra College, University of Calcutta, Kolkata 700029, India.

c. Chemical Sciences Division, Saha Institute of Nuclear Physics, Kolkata 700064, India.

d. Department of Physics, Assam University, Silchar-788011, Assam, India.

e. Department of Pharmaceutical Technology, Jadavpur University, Kolkata 700032, India.

*** Corresponding author, e-mail: devashish.sengupta@alumni.sydney.edu.au**

† These authors have contributed equally to the work.

Experimental Section

Materials and Methods

Thiophene-2-carboxaldehyde, propionic acid, methanol, 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide for (MTT), 2'7'dihydrodichlorofluoresceindiacetate (H2-DCFDA, Molecular Probe) (Sigma Aldrich), 4-formylphenyl propionate (SD Fine Chemicals), zinc acetate, dichloromethane, hexane (Merck), were used without further purification. Pyrrole (Sigma Aldrich) was freshly distilled before use. Silica gel (70-230 mm mesh, & 100 – 200 mm mesh, Merck) was employed for column chromatography. For the microwave-assisted synthesis, a Uwave-1000 microwave reactor (Sineo Microwave Chemistry Technology Co. Ltd. Shanghai, China) was used.

Optical Spectroscopy: UV-Visible absorption spectra were measured in a PerkinElmer LAMBDA 750 UV/Vis/NIR spectrophotometer taking the sample in 1 cm well-stoppered quartz cuvette (λ_{max} in nm) at different concentrations in DMF (Spectroscopic grade) or H_2O. Emission spectra were recorded on Fluoromax-4 spectroflouorometer (Horiba Scientific) at different concentration using DMF (Spectroscopic grade) or H_2O.

Fluorescence Lifetime Measurements: Fluorescence life times were measured using a time-correlated-single-photon counting (TCSPC) spectrophotometer (Horiba Jobin Yovin). The excitation wavelengths have been chosen to be 420 nm and emission wavelength chosen was the wavelength corresponding to the Q(0,0) band in the emission spectra from Table 1.1 respectively and MCP-PMT as a detector.

^{1}H-NMR and Mass Spectra

The ^{1}H nuclear magnetic resonance spectra were recorded either on Bruker (400 MHz) or Bruker Advance II (400 MHz) in $CDCl_3$ or DMSO-d6 (chemical shift in δ) solution with TMS as internal standard and the mass spectra were recorded using instruments micrOTOF-Q II or Agilent 6530 Accurate-Mass Q-TOF (version Q-TOF B.05.00, B5042.1).

Microwave-assisted synthesis of compounds T2(Et)2

In a 500 mL amber coloured three neck round bottom flask a mixture of thiophene-2-carboxaldehyde (3.87 mL, 0.035 mol, 2 eq), 4-hydroxybenzaldehyde (3.51 g, 0.029 mol, 2 eq) were dissolved in a mixture of propionic acid (150 mL) and propionic anhydride (50 mL) in a microwave system and pyrrole (4 mL, 0.057 mol, 4 eq) was added drop wise. The reaction mixture was stirred at 135 ^{0}C for 8 min using IR source as the sensor, with an irradiation power of 800 W. After completion, the excess propionic acid was removed by distillation under pressure. Neutralization of the crude product was achieved by using 0.5 M NH_3 solution and the solution was filtered. The residue thus obtained was first washed with copious amounts of water followed by cold diethyl ether. The dark crude product (~ 10 g) was loaded in a silica gel (70-230 mm mesh) column and eluted with 0.5% Et_3N (trimethyl amine) in 3% methanol in dichloromethane as the eluent. The porphyrin fractions were concentrated and then put to a second silica gel (70-230 mm mesh) column and eluted with 1% methanol in dichloromethane to provide pure **T2(Et)2** (351 mg, 10%).

Microwave-assisted synthesis of compounds T(Et)3

In a 500 mL amber coloured three neck round bottom flask a mixture of thiophene-2-carboxaldehyde (1.34 mL, 0.0144 mol, 1 eq), 4-hydroxybenzaldehyde (5.28 g, 0.043 mol, 3 eq) were dissolved in a mixture of propionic acid (150 mL) and propionic anhydride (50 mL) in a microwave system and pyrrole (4 mL, 0.057 mol, 4 eq) was added drop wise. The reaction mixture was stirred at 135 ^{0}C for 8 min using IR source as the sensor, with an irradiation power of 800 W. After completion, the excess propionic acid was removed by distillation under pressure. Neutralization of the crude product was achieved by using 0.5 M NH_3 solution and the solution was filtered. The residue thus obtained was first washed with copious amounts of water followed by cold diethyl ether. The dark crude product (~ 10 g) was loaded in a silica gel (70-230 mm mesh) column and eluted with 0.5% Et_3N (trimethyl amine) in 3% methanol in dichloromethane as the eluent. The porphyrin fractions were concentrated and then put to a second silica gel (70-230 mm mesh) column and eluted with 2% methanol in dichloromethane to provide pure **T(Et)3** (386 mg, 11%).

T2(Et)2: UV-Vis (DMF, 10 μM Solution), λ_{abs}/nm (ε/10^3 M^{-1} cm^{-1}): 655(11), (λ_{max}; Q-band), 596 (11) (λ_{max}; Q-band), 555(20) (λ_{max}; Q-band), 518 (33) (λ_{max}; Q-band), 422 (675) (λ_{max}; Soret band). Emission (DMF, 10 μM concentration), λ_{ex} = 422 nm (S-band): 650 nm Q(0,0), 716 nm Q(0,1) with Stokes shift 228 nm Q(0,0)-B(0,0);^{1}H-NMR (400 MHz, $CDCl_3$, 100 K), δ : 9.06 (s, 2H, pyrrole-H(β)), 9.04 (d, 2H, J = 5.50, pyrrole-H(β)), 8.87 (d, 2H, J = 5.50, pyrrole-H(β)), 8.85 (s, 2H, pyrrole-H(β)), 8.19 (d, 4H, *J* = 8.28 Hz, Ph-H(m)), 7.91(d, 2H, *J* = 3.28 Hz, Ty- H(m)), 7.84 (d, 2H, *J* = 4.96 Hz, Ty-H(o)), 7.49 (d, 4H, *J* = 8.28 Hz, Ph-H(o)), 7.50 (m, 2H, Ty-H(m')), 2.78 (q, 4H, -O-CH_2-), 1.42 (t, 6H, -CH_3), -2.71 (s, 2H, NH-pyrrole), 7.25 (s, $CDCl_3$), 1.52 (s, HOD); HRMS (ESI) Calculated for $C_{46}H_{34}N_4O_4S_2$ [M+H]+ m/z 771.2099, found 771.2101.

T(Et)3: UV-Vis (DMF, 10 μM Solution), λ_{abs}/nm (ε/10^3 M^{-1} cm^{-1}): 655(17), (λ_{max}; Q-band), 594 (15) (λ_{max}; Q-band), 553(26) (λ_{max}; Q-band), 517 (46) (λ_{max}; Q-band), 421 (737) (λ_{max}; Soret band). Emission (DMF, 10 μM concentration), λ_{ex} = 421 nm (S-band): 648 nm Q(0,0), 714 nm Q(0,1) with Stokes shift 227 nm Q(0,0)-B(0,0); ^{1}H-NMR (400 MHz, $CDCl_3$, 300 K), δ : 9.07-8.98 (8H, pyrrole-H(β)), 8.79 (d, 6H, *J* = 7.4 Hz, Ph-H(o)), 7.82 (d, 1H, Ty-H(m)), 8.13 (d, 1H, Ty-H(o)), 7.45 (m, 1H, Ty-H(m')), 7.40 (d, 6H, *J* = 7.4 Hz, Ph-H(m)), 2.72 (q, 6H, -O-CH_2-), 1.35 (t, 9H, -CH_3), -2.83 (s, 2H, NH-pyrrole), 7.19 (s, $CDCl_3$), 1.47 (s, HOD); HRMS (ESI) Calculated for $C_{51}H_{40}N_4O_6S$ [M+H]+ m/z 837.2747, found 837.2748.

Synthesis of compounds **T2(OH)2** and **T(OH)3**: The compounds **T2(OH)2 (**Yield: 170 mg 86%) and **T(OH)3** (Yield: 180 mg, 83%) were synthesized employing a previously described procedure.[1]

T2(OH)2: UV-Vis (DMF, 10 μM Solution), λ_{abs}/ nm (ε/10^3 M^{-1} cm^{-1}): 658(19), (λ_{max}; Q-band), 600 (16) (λ_{max}; Q-band), 560(33) (λ_{max}; Q-band), 522 (45) (λ_{max}; Q-band), 426 (783) (λ_{max}; Soret band). Emission (DMF, 10 μM concentration), λ_{ex} = 426 nm(S-band): 657 nm Q(0,0), 719 nm Q(0,1) with Stokes shift 231 nm Q(0,0)-B(0,0); ^{1}H-NMR (400 MHz, $CDCl_3$, 300 K), δ : 9.04 (s, 2H, pyrrole-H(β)), 9.02 (d, 2H, *J* = 4.64 Hz, pyrrole-H(β)), 8.86 (d, 2H, *J* = 4.64 Hz, pyrrole-H(β)), 8.84 (s, 2H, pyrrole-H(β)), 8.06 (d, 4H, *J* = 8.40 Hz, Ph-H(o)), 7.91 (d, 2H, *J* = 5.24 Hz, Ty-H(m)), 7.85 (d, 2H, *J* = 5.24 Hz, Ty-H(o)), 7.49 (m, 2H, Ty- H(m')), 7.22 (d, 4H, *J* = 8.40Hz, Ph-H(m)), 5.20 (s, 2H, Ph-OH), -2.67(s, 2H, NH-pyrrole), 7.26 (s, $CDCl_3$), 1.54 (s, HOD); HRMS (ESI) Calculated for $C_{40}H_{26}N_4O_2S_2$ [M+H]+ m/z 659.1575, found 659.1520.

T(OH)3: UV-Vis (DMF, 10 μM Solution), λ_{abs}/nm (ε/10^3 M^{-1} cm^{-1}): 654(19), (λ_{max}; Q-band), 595 (21) (λ_{max}; Q-band), 559(42) (λ_{max}; Q-band), 520 (48) (λ_{max}; Q-band), 425 (817) (λ_{max}; Soret band). Emission (DMF, 10 μM concentration), λ_{ex} = 425 nm (S-band): 655 nm Q(0,0), 717 nm Q(0,1) with Stokes shift 230 nm Q(0,0)-B(0,0); ^{1}H-NMR (400 MHz, $CDCl_3$, 300 K), δ = 7.91 (d, 1H, *J* = 3.36 Hz, Ty-H(m)), 9.14 (s, 3H, Ph-OH), 9.04 (d, 2H, *J* = 4.68 Hz, pyrrole-H(β)), 8.85 (d, 2H, *J* = 4.84 Hz, pyrrole-H(β)), 8.84 (s, 4H, H-β-pyrrole-H(β)), 8.06 (d, 6H, *J* = 8.44 Hz, Ph-H(o)), 7.83 (d, 1H, *J* = 4.31 Hz, Ty-H(o)), 7.49 (m, 1H, Ty-H(m′)), 7.21 (d, 6H, *J* = 8.40 Hz, Ph-H(m)), -2.71 (s, 2H, NH-pyrrole), 7.26 (s, $CDCl_3$), 1.55 (s, HOD); HRMS (ESI) Calculated for $C_{42}H_{28}N_4O_3S$ [M+H]+ m/z 669.1960, found 669.1961.

Synthesis of compounds T2(OH)2Zn and T(OH)3Zn: The synthetic methodology involved a previously published protocol.[2] The compounds **T2(OH)2Zn** (Yield: 88%, 90 mg) & **T(OH)3Zn** (Yield: 92 mg 87%) were obtained.[6]

T2(OH)2Zn: UV-Vis (DMF, 10 μM Solution), λ_{abs}/nm (ε/10^3 M^{-1} cm^{-1}): 627(21), (λ_{max}; Q-band), 605(30) (λ_{max}; Q-band), 564 (67) (λ_{max}; Q-band), 430 (958) (λ_{max}; Soret band). Emission (DMF, 10 μM concentration), λ_{ex} = 430 nm (S-band): 616 nm Q(0,0), 656 nm Q(0,1) with Stokes shift 186 nm Q(0,0)-B(0,0); ^{1}H-NMR (400 MHz, DMSO-d_6, 300 K), δ = 9.90(d, 2H, Ph-OH), 8.98 (s, 2H, pyrrole-H(β)), 8.96 (d, 2H, *J* = 4.8 Hz, pyrrole-H(β)), 8.84 (d, 2H, *J* = 4.8 Hz, pyrrole-H(β)), 8.83 (s, 2H, pyrrole-H(β)), 8.11 (d, 4H, *J* = 6.40 Hz, Ph-H(o)), 7.97 (d, 4H, *J* = 8.40 Hz, Ph-H(m)), 7.94 (d, 2H, *J* = 5.20 Hz, Ty-H(m)), 7.67 (m, 2H, Ty-H(m′)), 7.57 (m, 2H, *J* = 5.20 Hz, Ty-H(o)), 3.34 (s, DMSO-d_6), 2.51 (s, HOD); HRMS (ESI) Calculated for $C_{40}H_{24}N_4O_2S_2Zn$ [M+H]+ m/z 721.0710, found 721.0711.

T(OH)3Zn: UV-vis (DMF, 10 μM Solution), λ_{abs}/nm (ε/10^3 M^{-1} cm^{-1}): 628(13), (λ_{max}; Q-band), 604(28) (λ_{max}; Q-band), 562(58) (λ_{max}; Q-band), 429 (922) (λ_{max}; Soret band). Emission (DMF, 10 μM concentration), λ_{ex} = 429 nm (S-band): 618 nm Q(0,0), 657 nm Q(0,1) with Stokes shift 189 nm Q(0,0)-B(0,0). ^{1}H-NMR (400 MHz, DMSO-d6, 300 K), δ = 9.05-8.33 (8H, pyrrole-H(β)), 8.10 (d, 1H, *J* = 5.24 Hz, H-m-Ty), 7.61 (m, 1H, H-o-Ty), 7.95 (m, 1H, H-m′-Ty), 8.20 (d, 6H, *J* = 8.40 Hz, H-o-Ph), 7.23 (d, 6H, *J* = 8.44 Hz, H-m-Ph), 9.90 (d, 3H, OH-Ph), 3.34 (s, DMSO-d_6), 2.51 (s, HOD); HRMS (ESI) Calculated for $C_{42}H_{26}N_4O_3SZn$ [M+H]+ m/z 731.1095, found 731.1094.

Synthesis of final target compounds **T2(OH)2M**, **T(OH)3M**, **T2(OH)2MZn** and **T(OH)3MZn**: The compounds were synthesized employing a previously published protocol.[1]

T2(OH)2M: UV-Vis (DMF, 10 μM Solution), λ_{abs}/nm (ε/10^3 M^{-1} $cm^{\square 1}$): 653 (62), (λ_{max}; Q-band), 612 (89) (λ_{max}; Q-band), 565 (120) (λ_{max}; Q-band), 516 (130) (λ_{max}; Q-band), 430 (981) (λ_{max}; Soret band). Emission (DMF, 10 μM concentration), λ_{ex} = 430 nm (S-band): 665 nm Q(0,0), 724 nm Q(0,1) with Stokes shift 235 nm Q(0,0)-B(0,0); ^{1}H-NMR (400 MHz, DMSO-d6, 300 K), δ = 9.89 (s, 2H, OH-Ph), 8.98 (s, 2H, pyrrole-H(β)), 8.96 (d, 2H, *J* = 4.80 Hz, pyrrole-H(β)), 8.85 (d, 2H, *J* = 4.80 Hz, pyrrole-H(β)), 8.82 (s, 2H, pyrrole-H(β)), 8.10 (d, 4H, *J* = 8.40 Hz, Ph-H(o)), 7.97 (d, 4H, *J* = 8.40 Hz, Ph-H(m)), 7.93 (d, 2H, *J* = 3.40 Hz, Ph-

H(o)), 7.57 (m, 2H, Ph-H(m)), 7.18 (d, 2H, *J* = 7.60 Hz, Ph-H(m′), 2.93 (s, 6H, Ty-CH3), -2.83 (s, 2H, NH-pyrrole), 3.34 (s, HOD), 2.50 (s, DMSO); HRMS (ESI) Calculated for $C_{42}H_{32}N_4O_2S_2^{2+}$ [M]2+ m/z 344.0978, found 344.0978.

T(OH)3M: UV-Vis (DMF at 10 µM Solution, λ_{abs}/nm ($\varepsilon/10^3\ M^{-1}\,cm^{-1}$): 653(38), ($\lambda_{max}$; Q-band), 604 (46) ($\lambda_{max}$; Q-band), 562 (70) ($\lambda_{max}$; Q-band), 518 (76) ($\lambda_{max}$; Q-band), 426 (934) ($\lambda_{max}$; Soret band). Emission (DMF at 10 µM concentration), λ_{ex} = 426 nm (S-band): 664 nm Q(0,0), 725 nm Q(0,1) with Stokes shift 238 nm Q(0,0)-B(0,0); ^{1}H-NMR (400 MHz, DMSO-d_6, 300 K), δ = 10.01 (s, 3H, Ph-OH), 9.04-8.82 (8H, pyrrole-H(β)), 8.20 (d, 1H, *J* = 4.20 Hz, Ty-H(o)), 8.02 (d, 6H, J = 8.40 Hz, Ph-H(o)), 7.95 (d, 1H, *J* = 4.20 Hz, Ty-H(m)), 7.62 (m, 1H, Ty-H(m′)), 7.22 (d, 6H, *J* = 8.40 Hz, Ph-H(m)), 2.89 (s, 3H, Ty-SCH_3), -2.79 (s, 2H, NH-pyrrole), 3.34 (s, HOD), 2.50 (s, DMSO-d_6); HRMS (ESI) Calculated for $C_{43}H_{31}N_4O_3S^+$ [M]+ m/z 683.2111, found 683.2090.

T2(OH)2MZn: UV-Vis (DMF, 10 µM Solution), λ_{abs}/nm ($\varepsilon/10^3\ M^{-1}\,cm^{-1}$): 614 (144), ($\lambda_{max}$; Q-band), 563 (175) ($\lambda_{max}$; Q-band), 434 (1031) ($\lambda_{max}$; Soret band). Emission (DMF, 10 µM concentration), λ_{ex}= 434 nm (S-band): 620 nm Q(0,0), 665 nm Q(0,1) with Stokes shift 186 nm Q(0,0)-B(0,0). ^{1}H-NMR (400 MHz, DMSO-d_6, 300 K), δ = 9.91 (s, 2H, Ph-OH), 8.98 (s, 2H, pyrrole-H(β)), 8.96 (d, 2H, *J* = 4.40 Hz, pyrrole-H(β)), 8.85 (d, 2H, *J* = 4.80 Hz, pyrrole-H(β)), 8.82 (s, 2H, pyrrole-H(β)), 8.11 (d, 2H, *J* = 5.2 Hz, Ty-H(o)), 7.96 (d, 4H, *J* = 8.40 Hz, Ph-H(o)), 7.94 (d, 2H, *J* = 3.60 Hz, Ty-H(m)), 7.57 (m, 2H, Ty-H(m′)), 7.18 (d, 4H, *J* = 8.40 Hz, Ph-H(m)), 5.76 (s, 6H, Ty-SCH_3), 2.510 (s, DMSO-d_6), 3.36 (s, HOD) and HRMS (ESI) Calculated for $C_{42}H_{30}N_4O_2S_2Zn^{2+}$ [M]2+ m/z 375.0545, found 375.0546.

T(OH)3MZn: UV-Vis (DMF, 10 µM Solution), λ_{abs}/nm ($\varepsilon/10^3\ M^{-1}\,cm^{-1}$): 608 (141), ($\lambda_{max}$; Q-band), 548 (200) ($\lambda_{max}$; Q-band), 431 (980) ($\lambda_{max}$; Soret band). Emission (DMF, 10 µM solution), λ_{ex} = 431 nm(S-band): 619 nm Q(0,0), 664 nm Q(0,1) with Stokes shift 188 nm Q(0,0)-B(0,0); ^{1}H-NMR (400 MHz, DMSO-d_6, 300 K), δ = 9.03-8.82 (8H, pyrrole-H(β)), 8.04 (d, 1H, J = 5.20 Hz, H-m-Ty) 8.17 (d, 1H, *J* = 5.20 Hz, H-o-Ty), 7.71 (m, 1H, H-m′-Ty), 7.91 (d, 6H, *J* = 8.40 Hz, H-o-Ph), 7.05 (d, 6H, *J* = 8.40 Hz, H-m-Ph), 9.92 (d, 3H, Ph-OH), 5.72 (d, 3H, Ty-S CH_3); HRMS (ESI) Calculated for $C_{43}H_{29}N_4O_3SZn$ [M]+ m/z 745.1246, found 745.1244.

Biological assay:

Cell lines: Human cancer cell line, A549 (non-small cell lung cancer cell line), L-132 (normal lung cell line) were collected from National Centre for Cell Science, Pune, India and were cultured in Dulbecco Modified Eagle Medium (DMEM). Human normal peripheral blood mononuclear cell (PBMC) was isolated from normal healthy human and was cultured in Roswell Park Memorial Institute medium (RPMI-1640). All these cells are cultured with 10% heat-inactivated FBS and 1%antibiotic (PSN) and maintained at 37 ^{0}C with 5% CO_2 in a humidified incubator. Adherent cells (A549, L-132) were harvested with 0.025% trypsin and 0.52 mM EDTA in phosphate buffer saline, plated at required cell numbers and allowed to adhere for minimum ~ 24h before treatment.

Treatment with the synthesized compounds: For MTT assay, the cell lines were exposed to the various synthesized compounds (**T(OH)3MZn**, **T2(OH)2M**, **T(OH)3M** and **T2(OH)2MZ**) with 1.25, 2.5, 5, 10 and 20 μM concentrations at 37 ^{0}C in DMEM or RPMI-1640 supplemented with the serum. As a positive control, an equal volume of medium was added to the untreated cells.

MTT assay

The *in vitro* cytotoxicity of the photosensitizers **T2(OH)2M**, **T(OH)3M**, **T2(OH)2MZn** and **T(OH)3MZn** was measured through MTT assay at 2.5, 5, 10 and 20 μM concentration. Their effect on three different cell lines, namely, human lung cancer cell line A549 along with normal lung cells L-132 and PBMCs as control was evaluated by performing MTT assay under both photodynamic and dark conditions. A Philips Essential Master PL-L 36W/865/4P linear compact fluorescent lamp (λ = 400–700 nm, Luminous Efficacy¼ 80 lm/W) placed at a distance of 10 cm for 30 min served as the radiation source. Light received at the surface of the 96 well plates was approximately 16498851 lm s.[1-2]

Reactive oxygen species (ROS) activity assay

Intracellular ROS generation in cells were assessed fluorometrically[3] using 2$^/$7$^/$dihydrodichlorofluoresceindiacetate (H2-DCFDA,Molecular Probe). ~1 ×10^3 cells were treated with 7 μM of **T2(OH)2MZn** for 0, 4, 6, 12 and 24h in presence or absence of light. The cells were then washed with phosphate buffer saline(PBS) and further incubated with 10 μM H2-DCFDA for 30 min at 37 °C in dark condition. Thereafter the stained cells were washed twice in PBS at room temperature for 5 min each. The fluorescence measured at excitation and emission wavelengths of the oxidized form at 504 nm and 529 nm, respectively. Hydrogen peroxide (H_2O_2) treated cells were taken as the loading control.[4]

Determination of intracellular GSH content

A549 cells were treated with 7μM of **T2(OH)2MZn (4, 6, 12 h)** and also left untreated. Thereafter both the light treated and untreated cells were taken to determine intracellular GSH content. Briefly, drug-treated and -untreated cells were taken and cell extracts were prepared. 100 μL cell extract was added with 400 μL sulphosalicylic acid and after centrifugation, 500 μL supernatant was taken and mixed with 4.5 ml DTNB solution. Thereafter immediate spectroscopic measurement was recorded against reagent blank (4.5 ml DTNB + 500 μL distilled water).[4]

DFT Studies:

The molecular geometries of compounds synthesized here, **T2(OH)2M**, **T(OH)3M**, **T2(OH)2MZn** and **T(OH)3MZn** were fully optimized in two electronic states in vacuum using the B3LYP hybrid functional of the density functional theory (DFT) and the 6-31G* basis set, as implemented in the Gaussian 09 quantum chemistry package.[5] Frequency calculations at the same level of theory were also performed on each optimized geometry to confirm the genuineness of the nature of minima. We note that the B3LP/6-31G* level of theory has been reported to provide structure and vibrational analysis of metalloporphyrin systems in good agreement with experimental data.[6] The single-triplet energy gap for all the compounds was also calculated. The Gauss View program[7] was used for visualization of structures and vibrational modes.

Reference:

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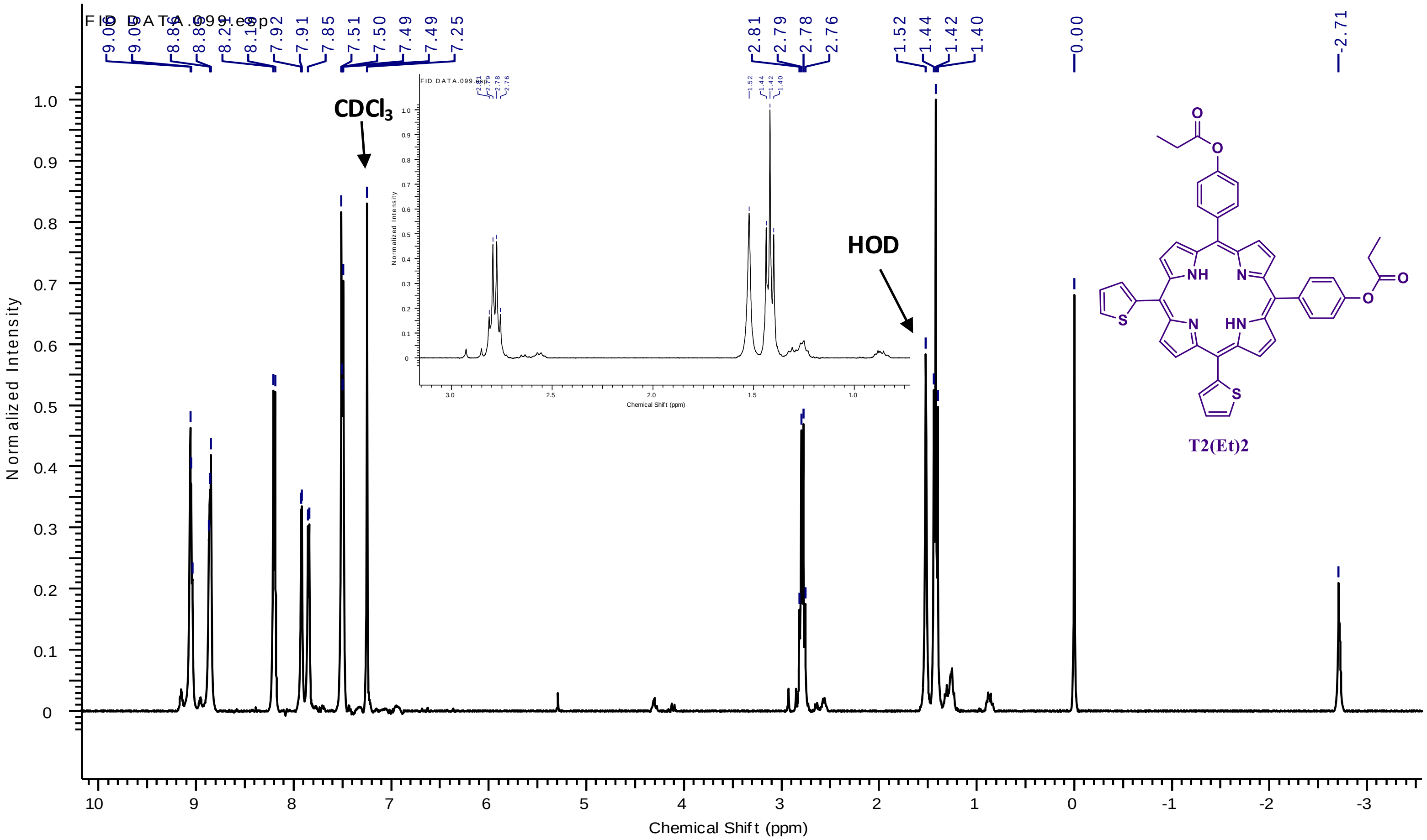
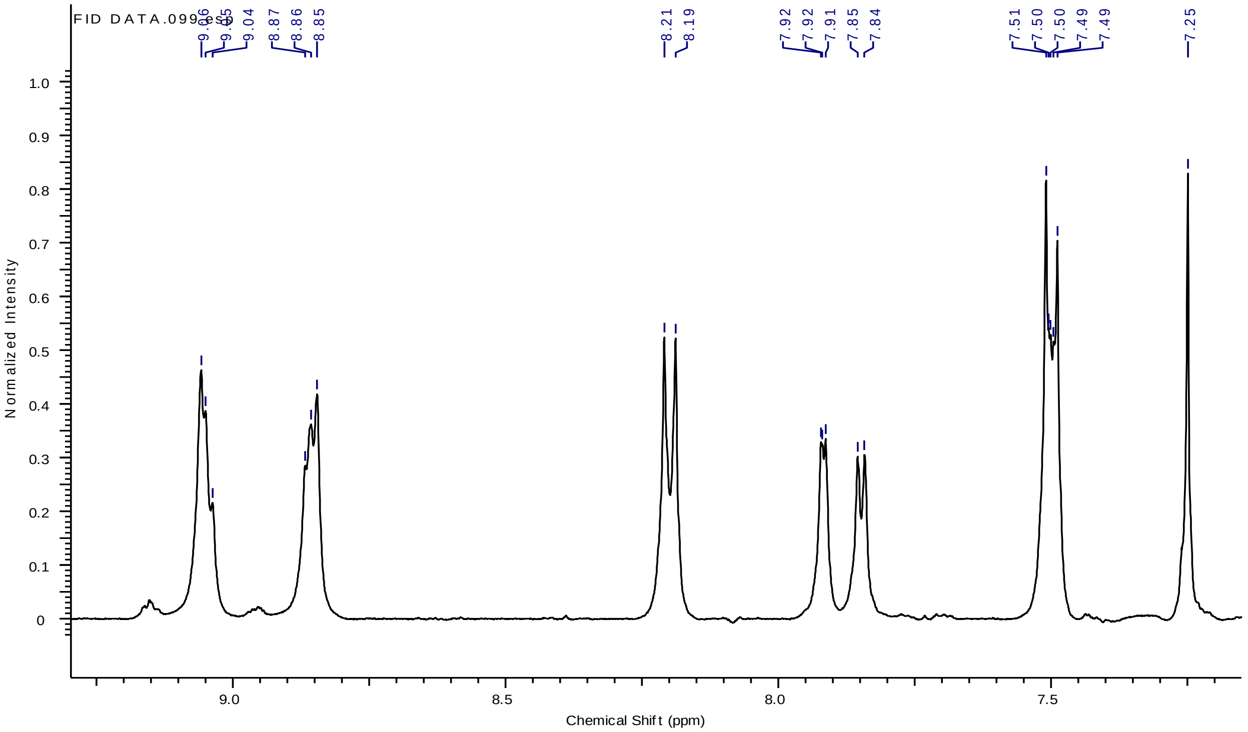
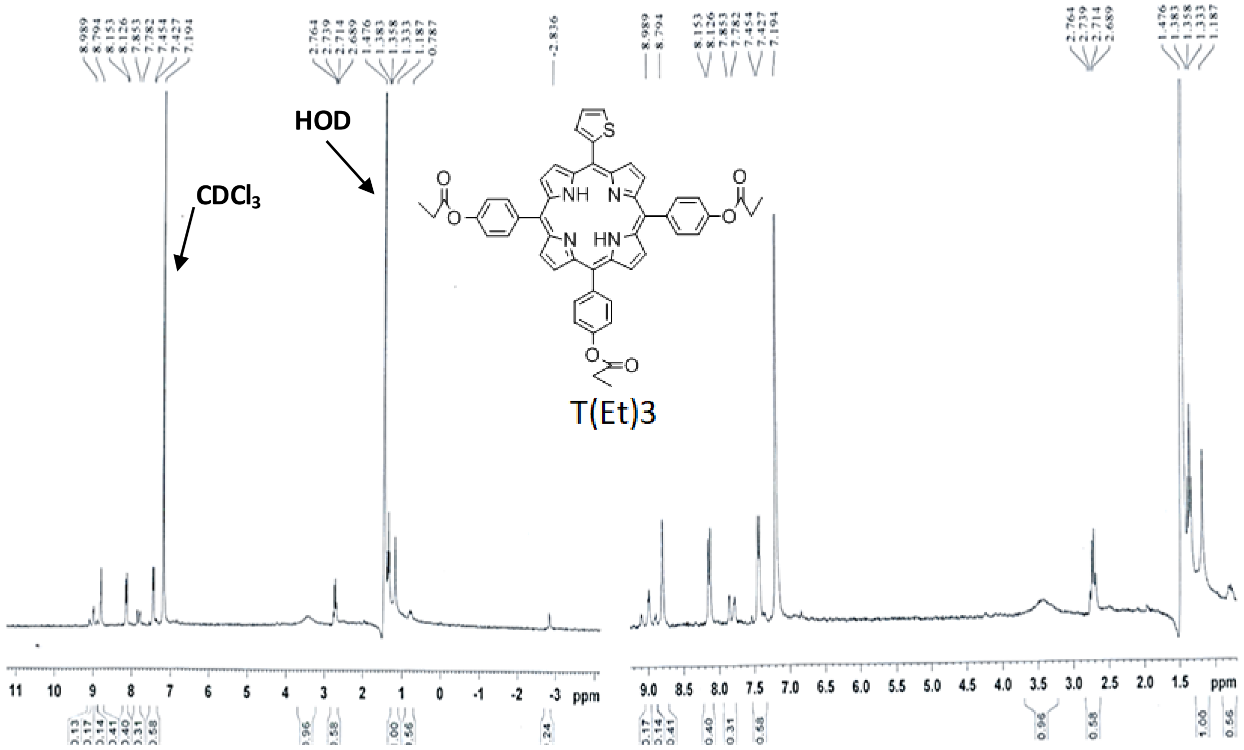
^{1}H-NMR Spectra:






8.989
8.794
8.153
8.126
7.853
7.782
7.454
7.427
7.194
2.764
2.739
2.714
2.689
1.476
1.383
1.358
1.333
1.187
0.787
-2.836
HOD
CDCl3
T(Et)3
11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 ppm
0.13
0.17
0.14
0.41
0.40
0.31
0.58
0.96
0.58
1.00
0.56
.24
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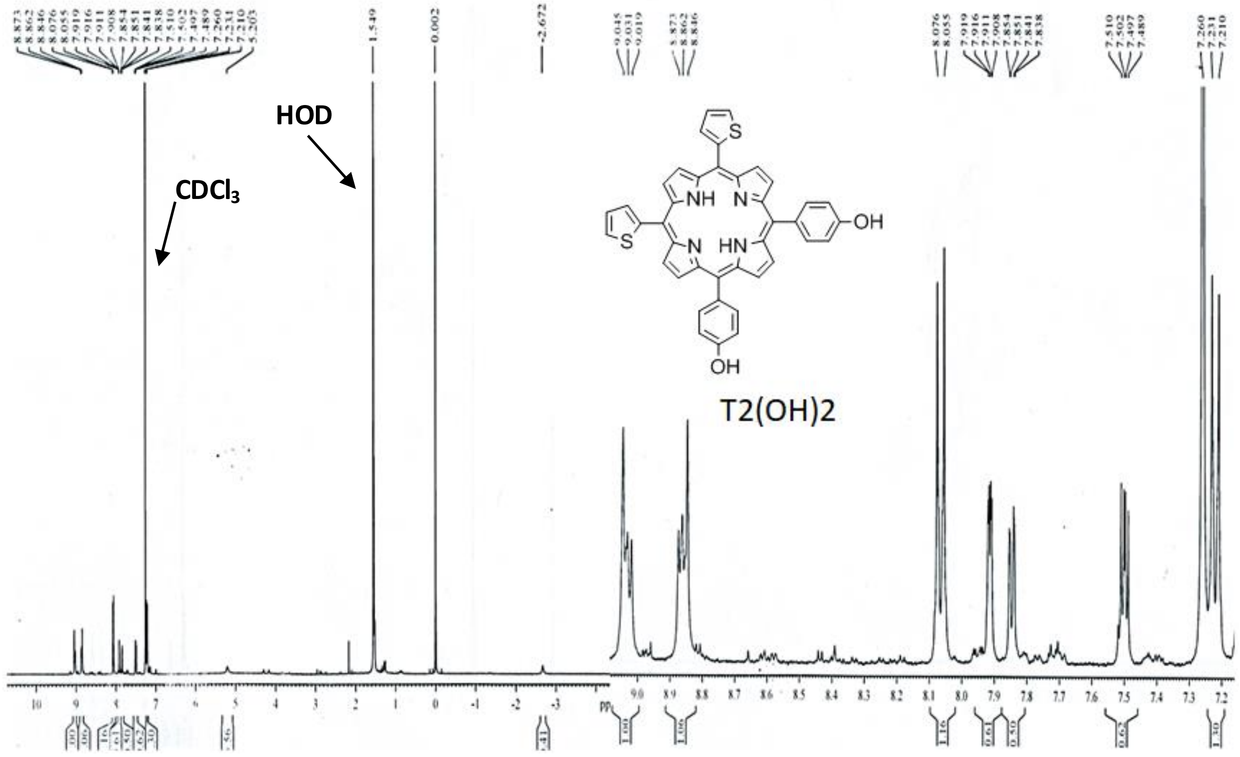
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CDCl$_3$
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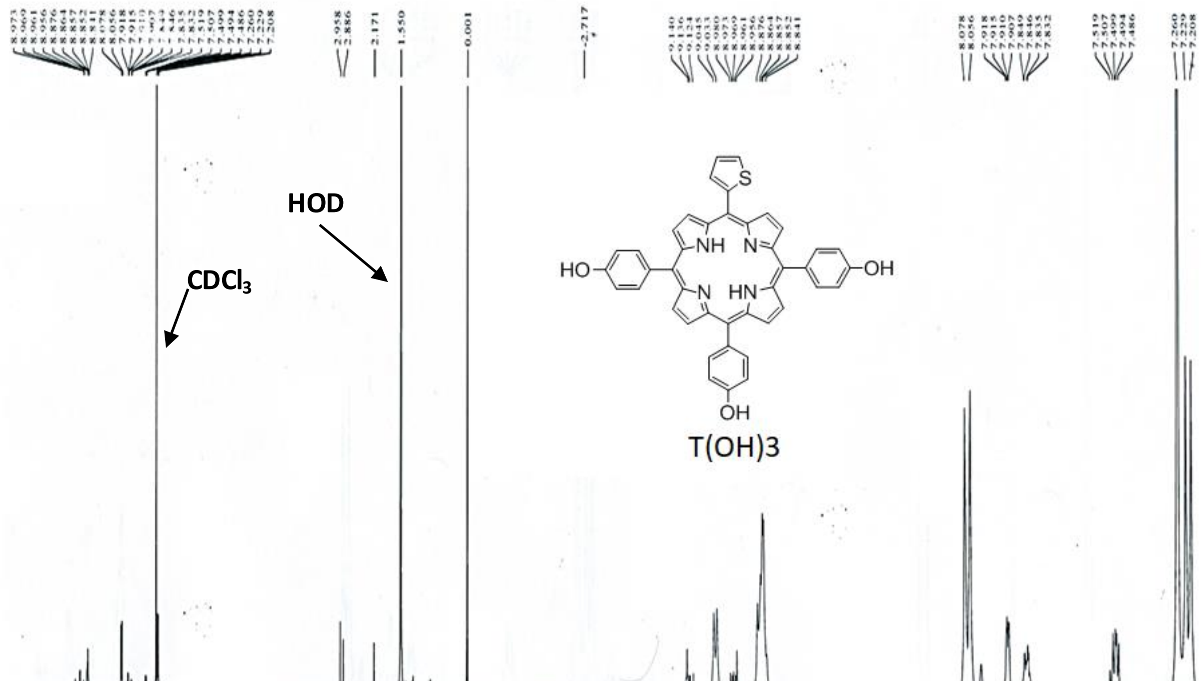
0.002
-2.672
9.045
9.031
9.019
8.873
8.862
8.846
8.076
8.055
7.919
7.916
7.911
7.908
7.854
7.851
7.841
7.838
7.510
7.502
7.497
7.489
7.260
7.231
7.210
5.203
1.00
1.06
1.16
0.61
0.50
0.62
1.30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7.915
7.910
7.907
7.846
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7.835
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7.486
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7.229
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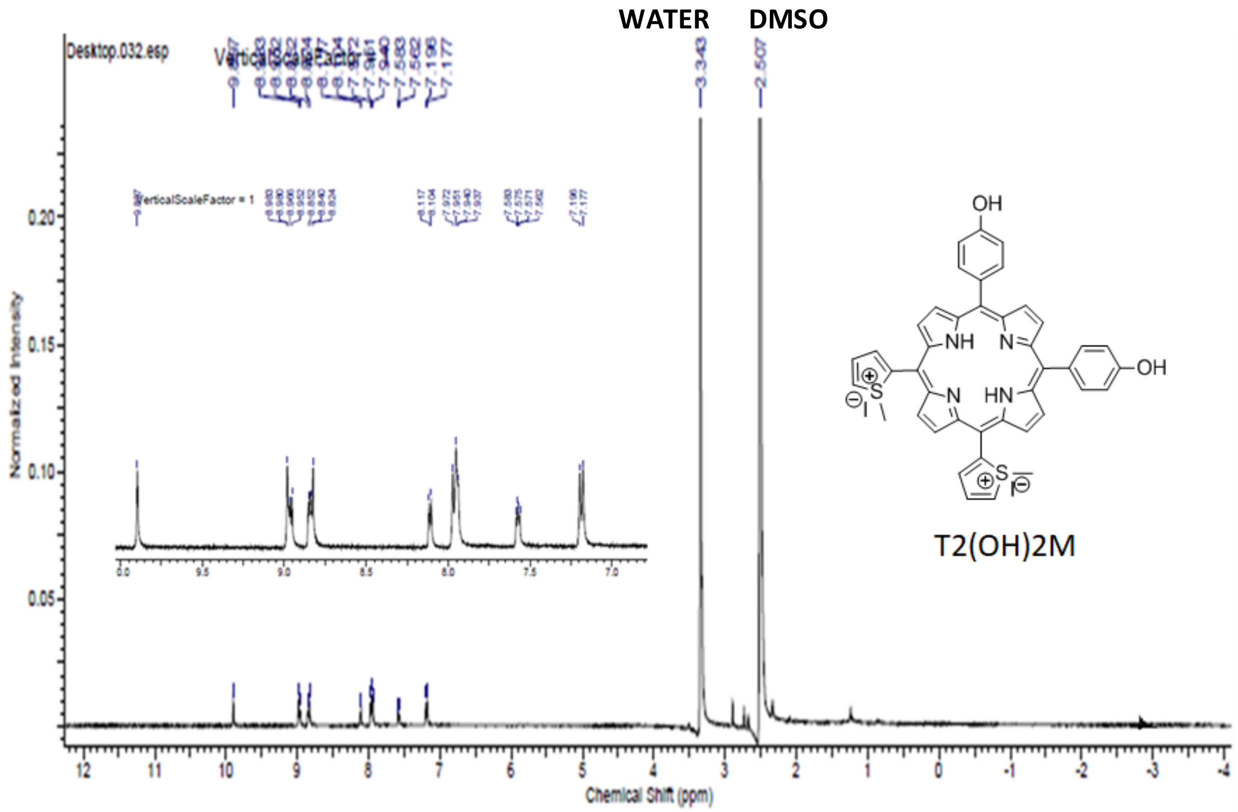
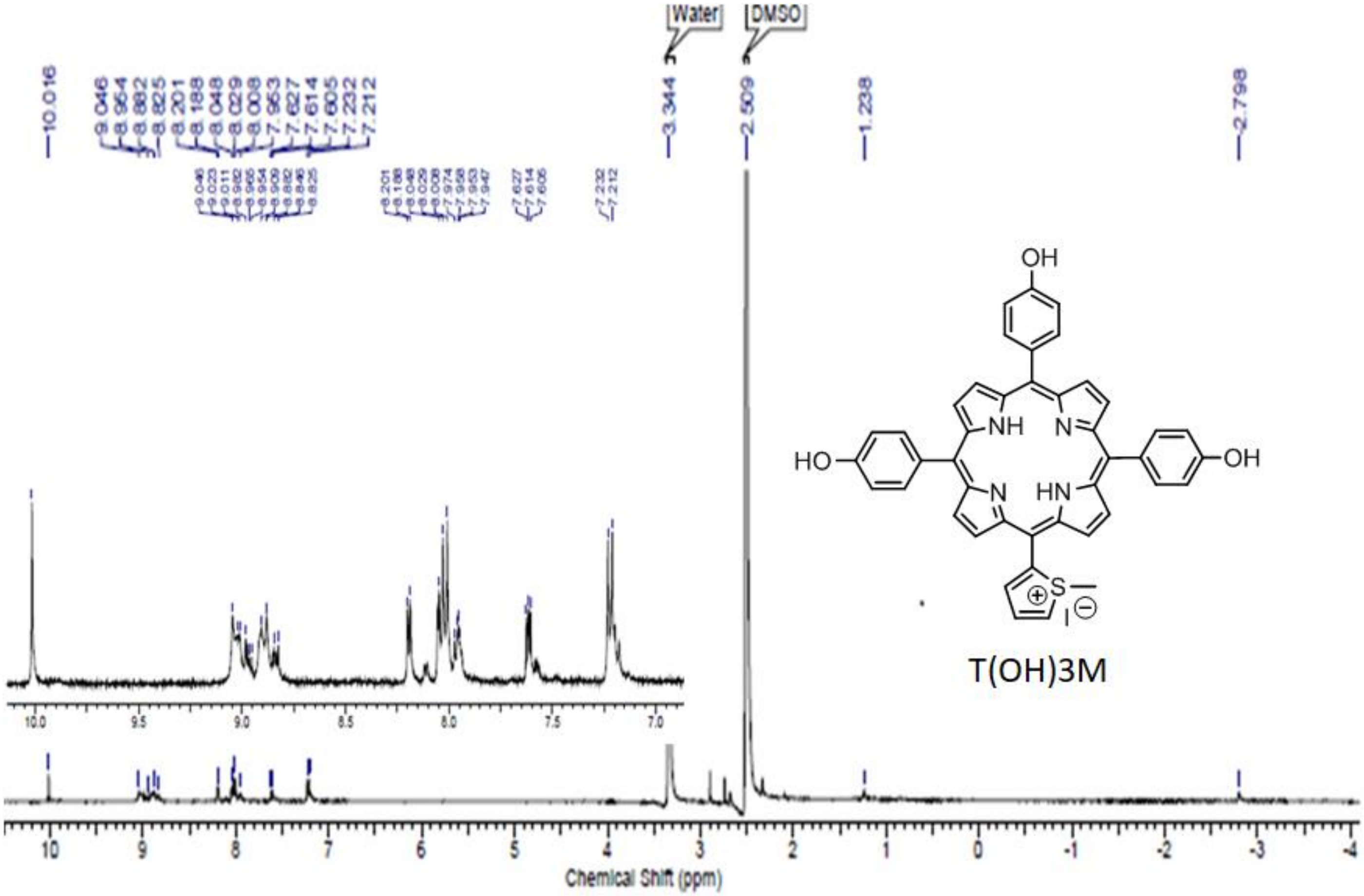
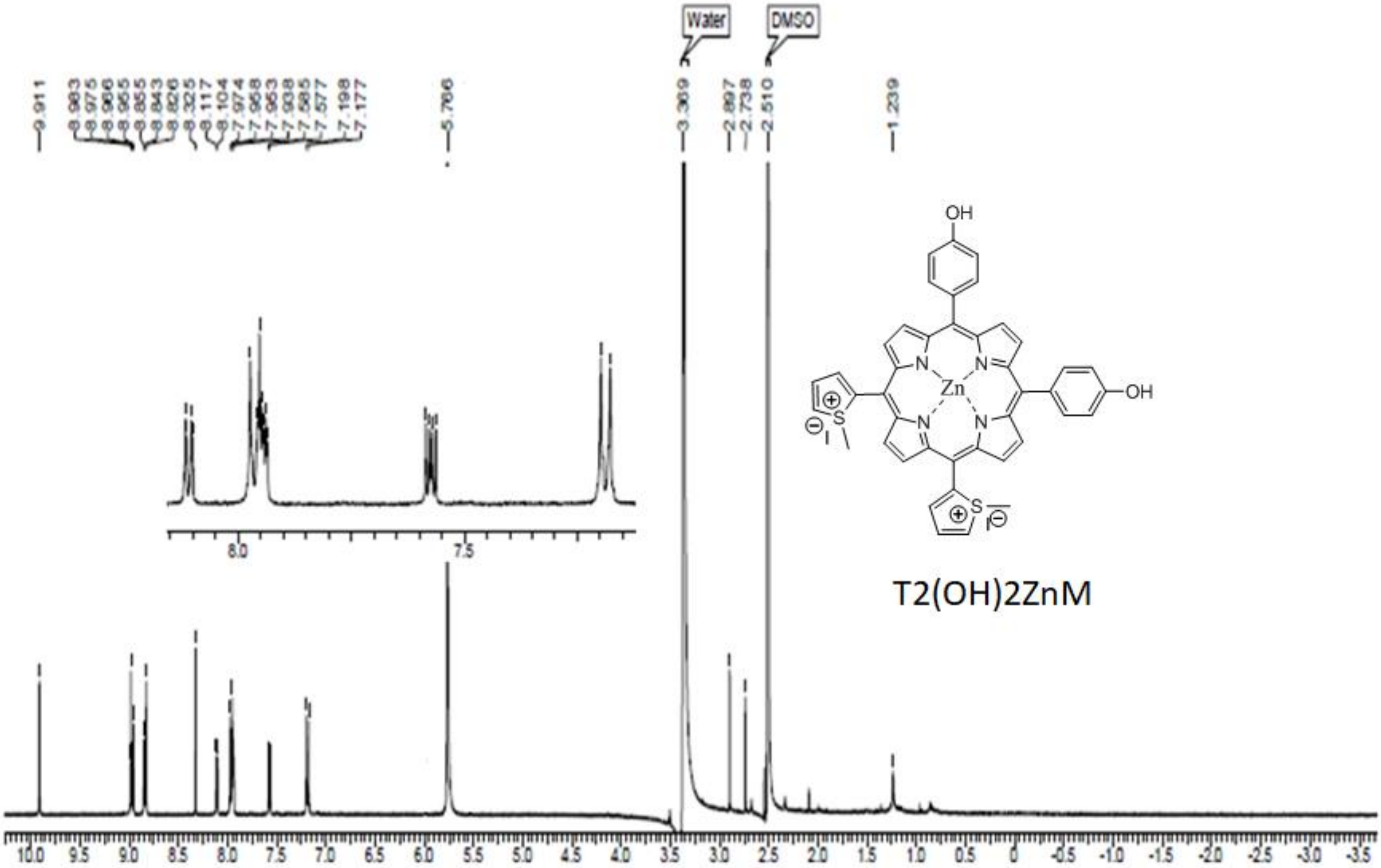
0.60



T2(OH)2M



T(OH)3M



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DMSO
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8.966
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8.855
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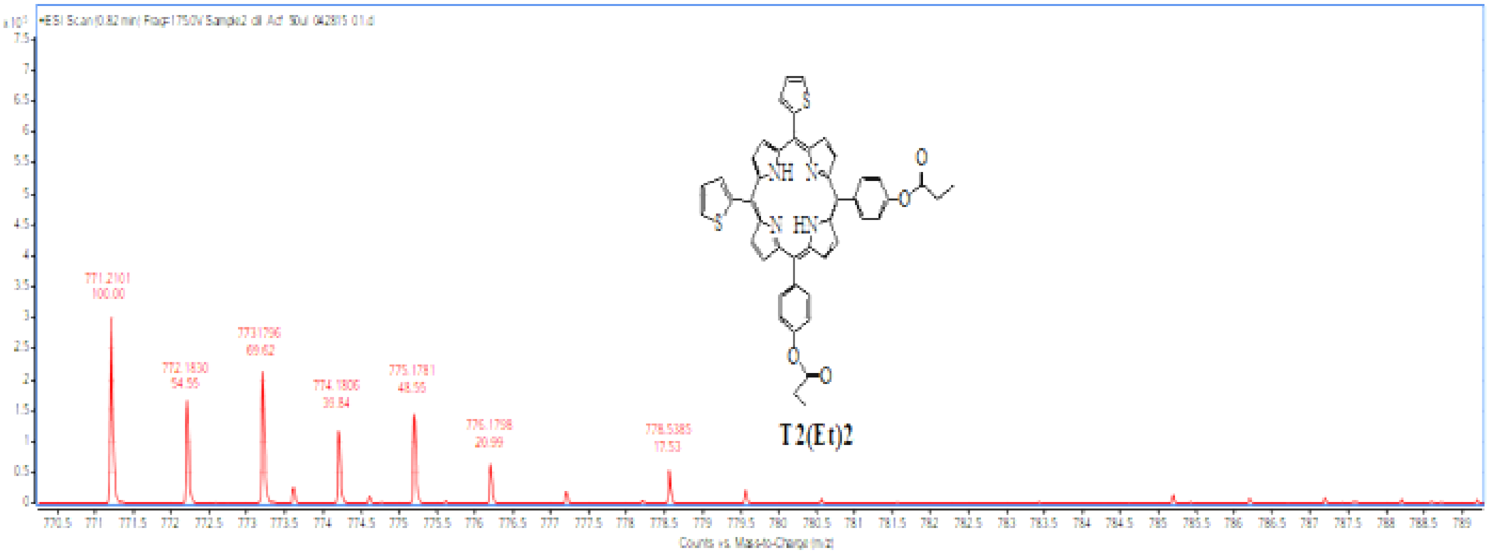
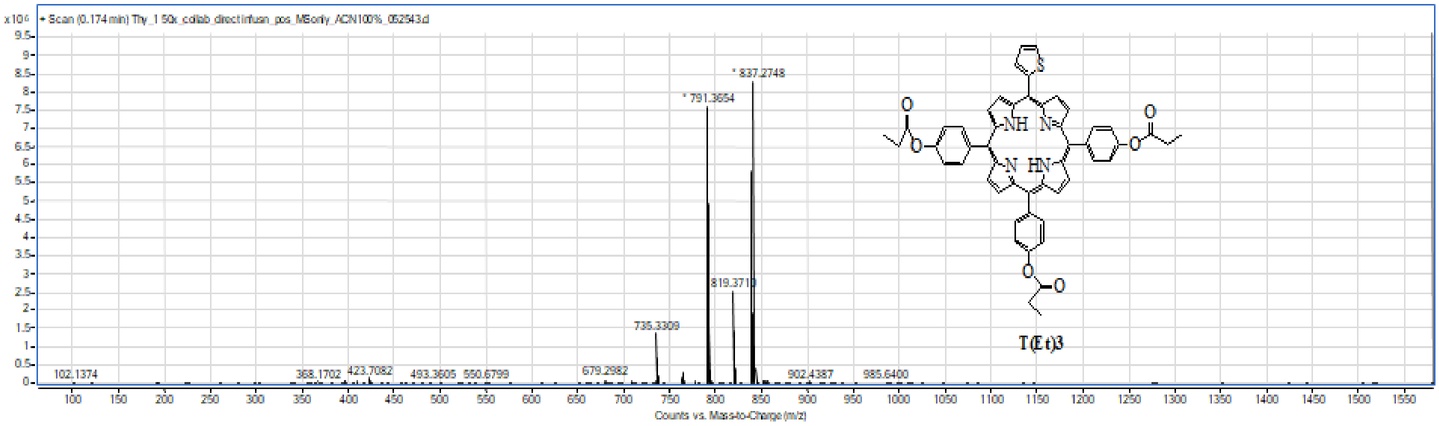
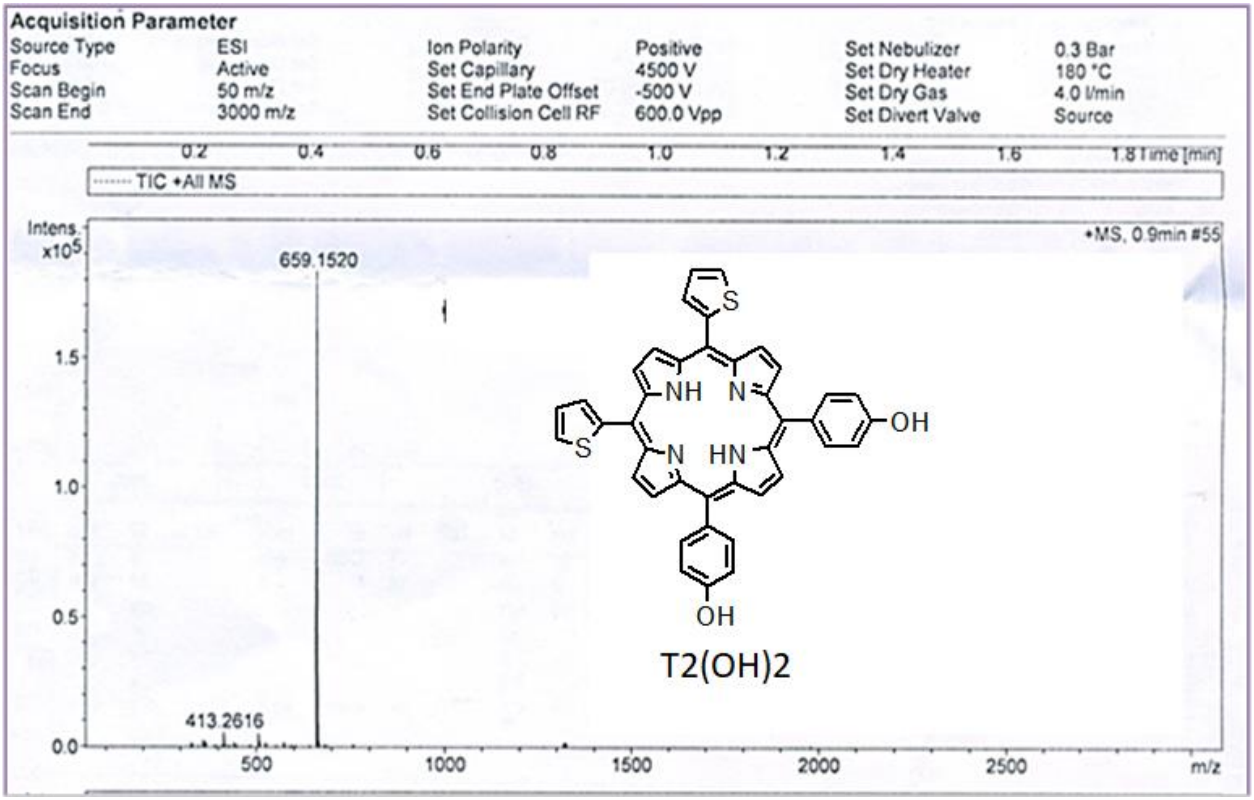
7.938
7.585
7.577
7.198
7.177
5.766
3.369
2.897
2.738
2.510
1.239
8.0
7.5
OH
OH
N
N
N
N
Zn
S
S
I
I
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5

T2(OH)2ZnM

Mass Spectra



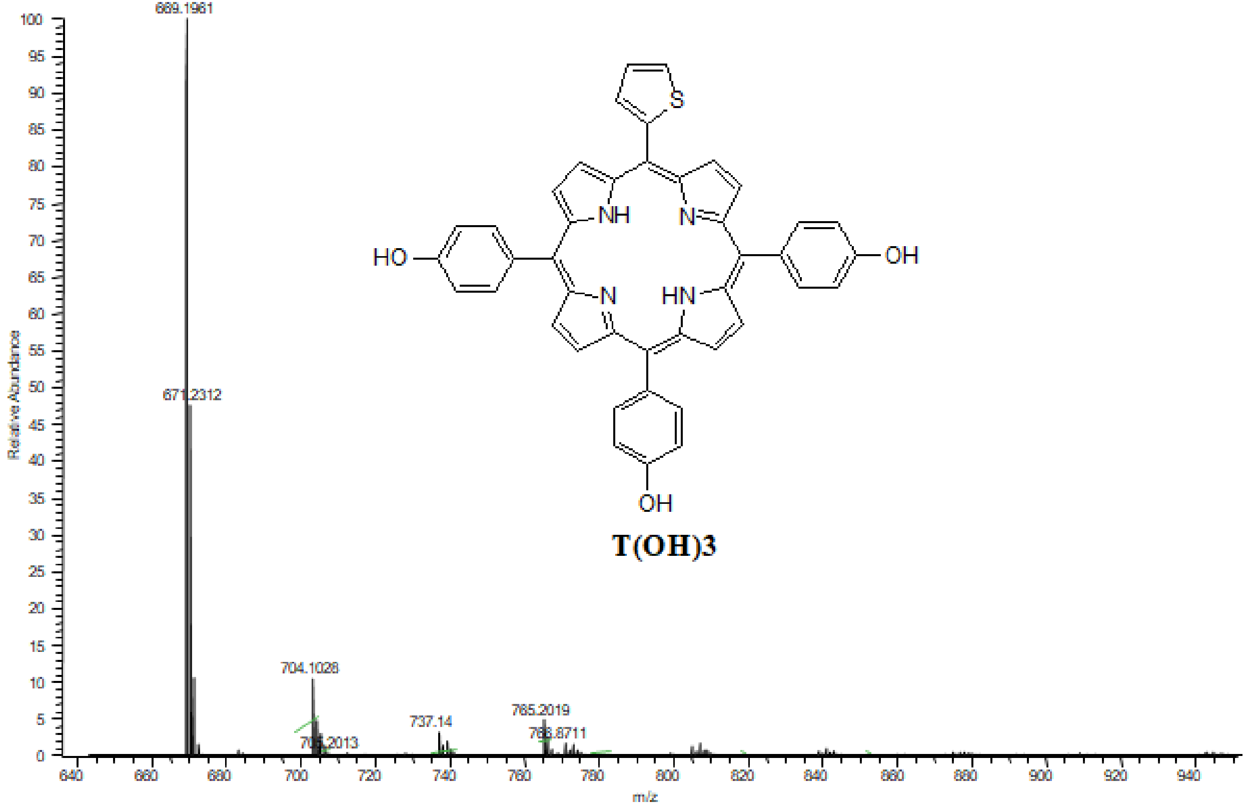




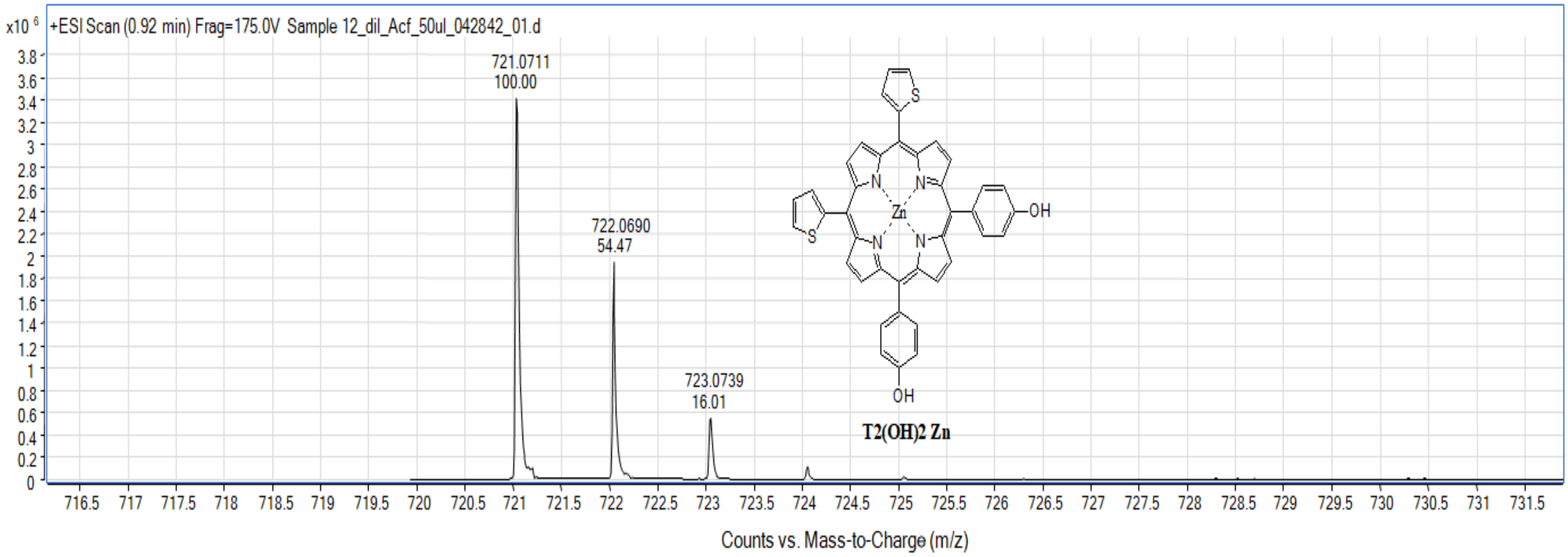
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

T2(OH)2



T(OH)3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3.6
3.4
3.2
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
721.0711
100.00
722.0690
54.47
723.0739
16.01
S
N
N
Zn
N
N
OH
S
OH
T2(OH)2 Zn
716.5
717
717.5
718
718.5
719
719.5
720
720.5
721
721.5
722
722.5
723
723.5
724
724.5
725
725.5
726
726.5
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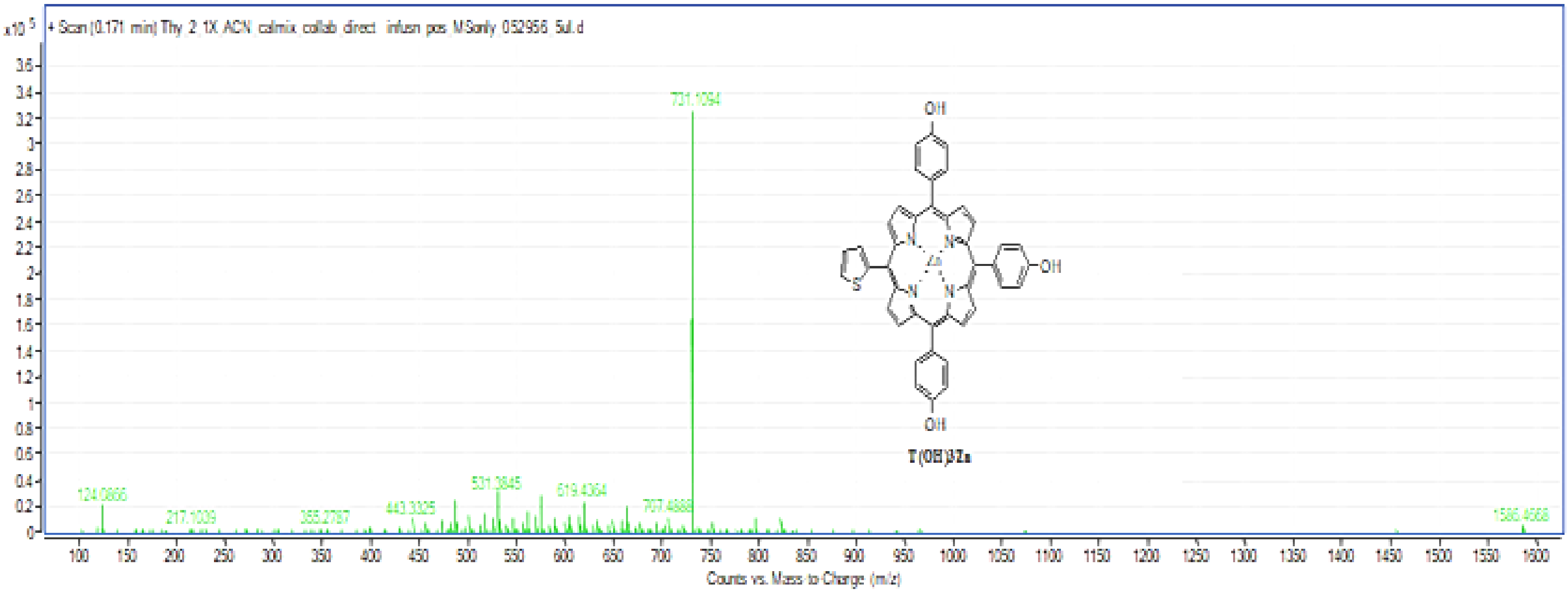
731
731.5
Counts vs. Mass-to-Charge (m/z)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+ Scan (0.171 min) Thy_2_1X_ACN_calmix_collab_direct_infusn_pos_MSonly_052956_5ul.d
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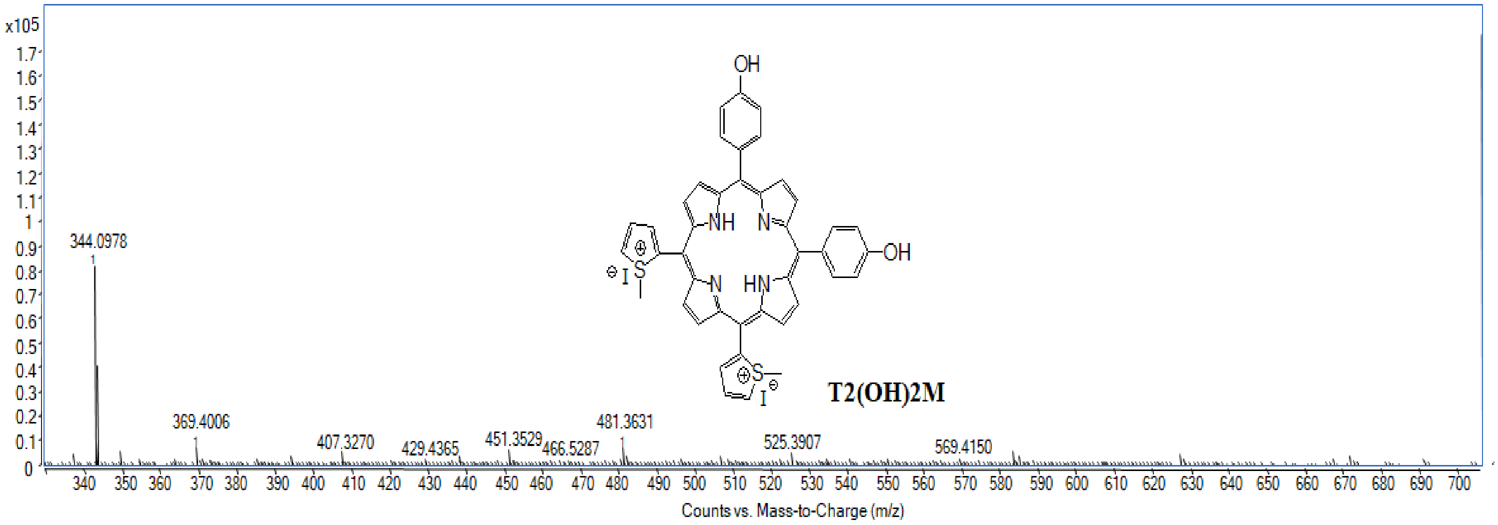
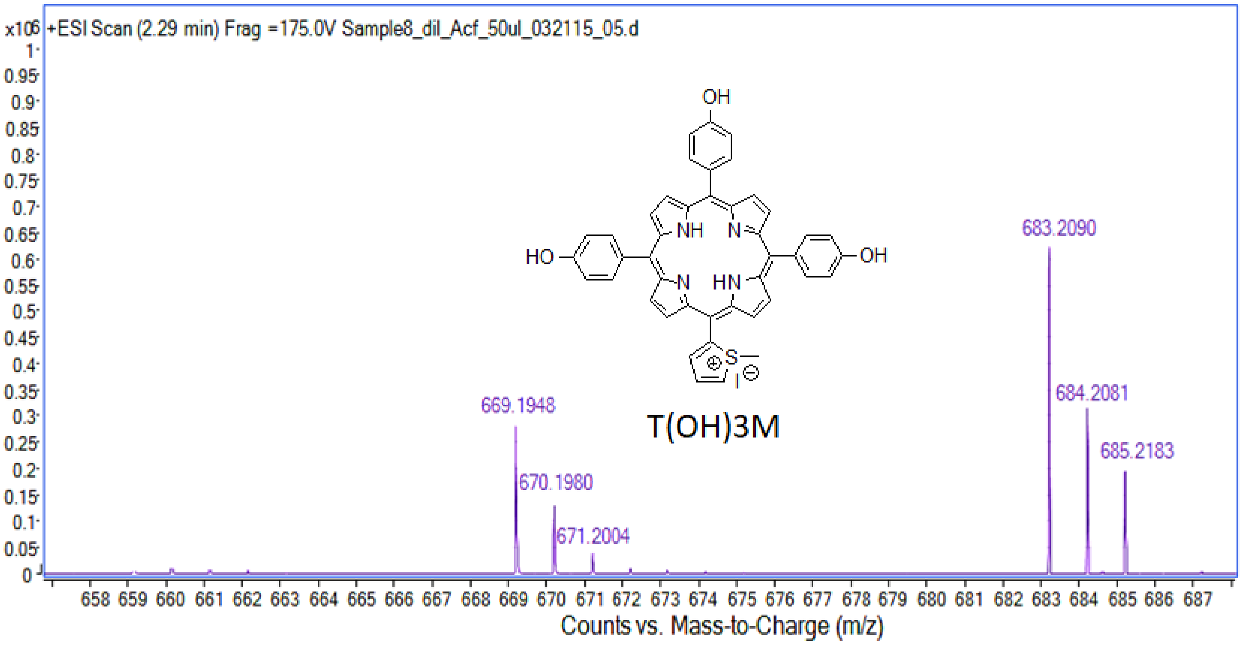
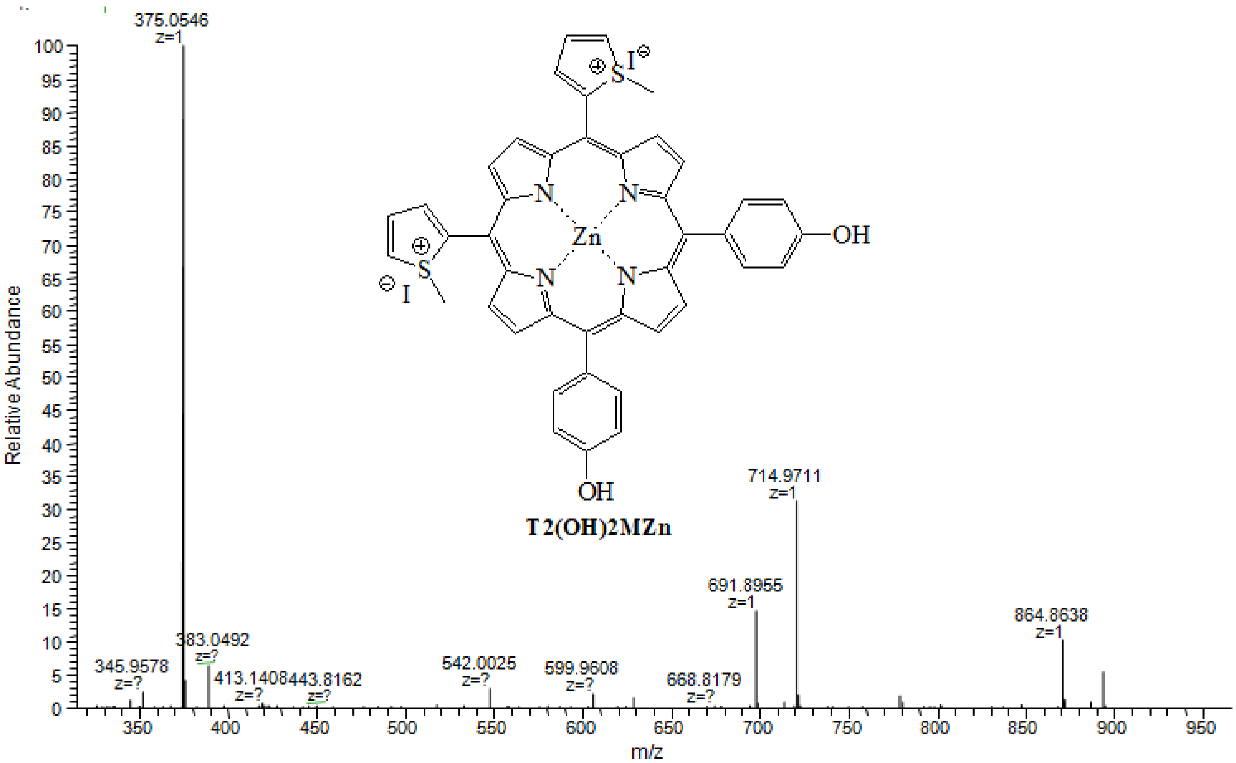
3.4
3.2
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
731.1094
124.0866
217.1039
355.2787
443.3325
531.3845
619.4364
707.4888
1586.4568
OH
N
N
Zn
N
N
S
OH
OH
T(OH)3Zn
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
1050
1100
1150
1200
1250
1300
1350
1400
1450
1500
1550
1600
Counts vs. Mass-to-Charge (m/z)



T2(OH)2M



T(OH)3M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90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
Relative Abundance
S
I
N
Zn
OH
T2(OH)2MZn
714.9711
z=1
691.8955
z=1
864.8638
z=1
383.0492
z=?
345.9578
z=?
413.1408
z=?
443.8162
z=?
542.0025
z=?
599.9608
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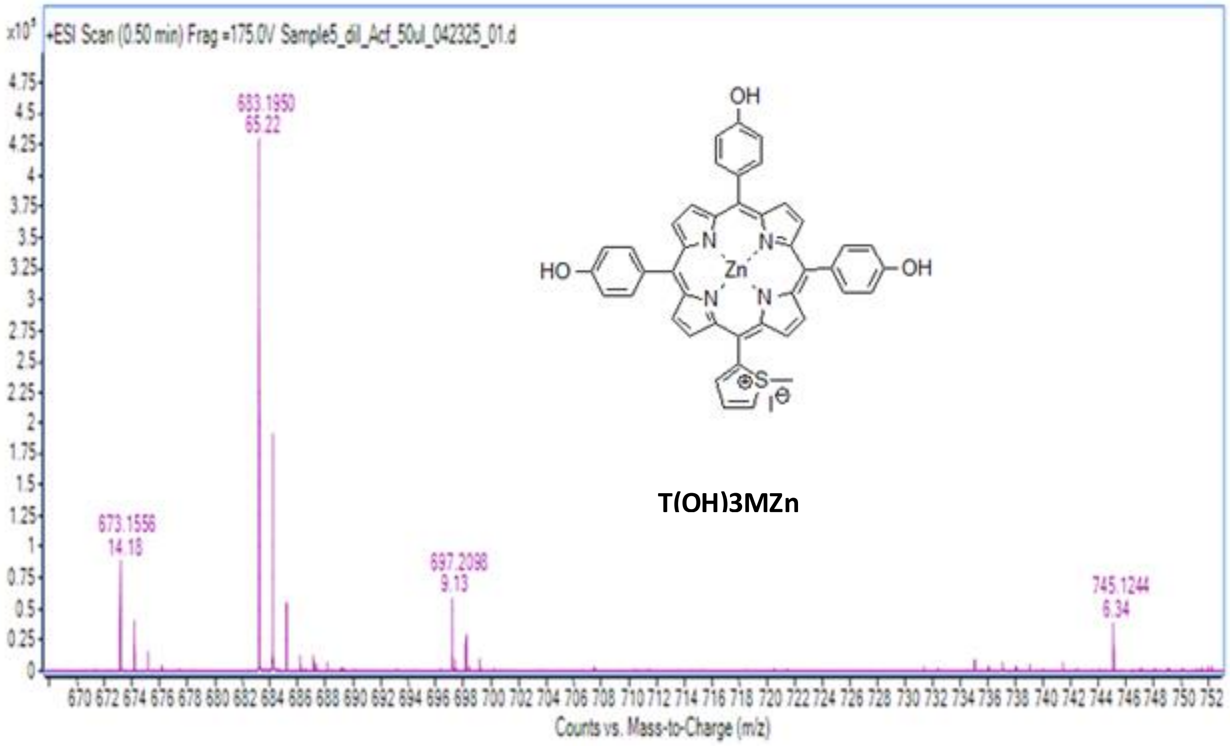
350
400
450
500
550
600
650
700
750
800
850
900
950
m/z


x10^5
+ESI Scan (0.50 min) Frag =175.0V Sample5_dil_Acf_50ul_042325_01.d
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4.5
4.25
4
3.75
3.5
3.25
3
2.75
2.5
2.25
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
683.1950
65.22
673.1556
14.18
697.2098
9.13
745.1244
6.34
OH
HO
OH
N
N
Zn
N
N
S
I
670 672 674 676 678 680 682 684 686 688 690 692 694 696 698 700 702 704 706 708 710 712 714 716 718 720 722 724 726 728 730 732 734 736 738 740 742 744 746 748 750 752
Counts vs. Mass-to-Charge (m/z)

T(OH)3MZn

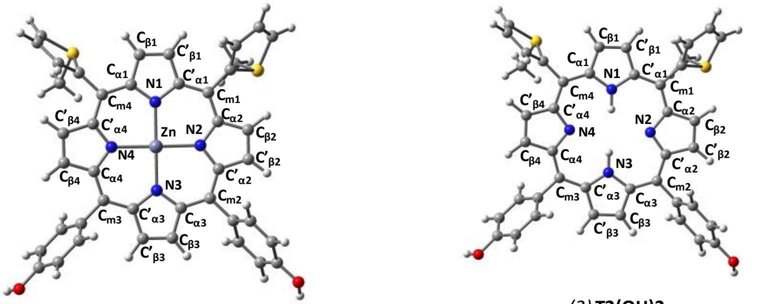
Table S1: Certain optimized bond lengths of different compounds determined at the B3LYP/6-31G* level of theory

Bond length (Å)	Compounds			
	T2(OH)2MZn	**T2(OH)2M**	**T(OH)3MZn**	**T(OH)3M**
N1-Zn	2.068	-	2.058	-
N2-Zn	2.045	-	2.052	-
N3-Zn	2.032	-	2.042	-
N4-Zn	2.049	-	2.040	-
N1-N3	4.100	4.235	4.100	4.238
N2-N4	4.094	4.088	4.091	4.084
$C_{\alpha1}$-$C_{\beta1}$	1.444	1.432	1.442	1.430
$C'_{\alpha1}$-$C'_{\beta1}$	1.445	1.433	1.446	1.433
$C_{\beta1}$-$C'_{\beta1}$	1.360	1.370	1.360	1.370
N1-$C_{\alpha1}$	1.377	1.377	1.387	1.386
N1-$C'_{\alpha1}$	1.376	1.376	1.367	1.368
$C_{\alpha2}$-$C_{\beta2}$	1.443	1.460	1.445	1.462
$C'_{\alpha2}$-$C'_{\beta2}$	1.441	1.457	1.440	1.455
$C_{\beta2}$-$C'_{\beta2}$	1.362	1.354	1.362	1.355
N2-$C_{\alpha2}$	1.369	1.357	1.366	1.350
N2-$C'_{\alpha2}$	1.383	1.376	1.387	1.382
$C_{\alpha3}$-$C_{\beta3}$	1.443	1.433	1.441	1.430
$C'_{\alpha3}$-$C'_{\beta3}$	1.443	1.433	1.442	1.430
$C_{\beta3}$-$C'_{\beta3}$	1.360	1.369	1.362	1.372
N3-$C_{\alpha3}$	1.377	1.374	1.374	1.372
N3-$C'_{\alpha3}$	1.376	1.374	1.378	1.376
$C_{\alpha4}$-$C_{\beta4}$	1.441	1.457	1.442	1.457
$C'_{\alpha4}$-$C'_{\beta4}$	1.444	1.460	1.441	1.458
$C_{\beta4}$-$C'_{\beta4}$	1.361	1.354	1.362	1.354
N4-$C_{\alpha4}$	1.384	1.375	1.379	1.371
N4-$C'_{\alpha4}$	1.369	1.357	1.374	1.362
$C'_{\alpha1}$-C_{m1}	1.413	1.413	1.425	1.423
$C_{\alpha2}$-C_{m1}	1.419	1.426	1.422	1.432
$C'_{\alpha2}$-C_{m2}	1.408	1.410	1.400	1.400
$C_{\alpha3}$-C_{m2}	1.412	1.413	1.413	1.416
$C'_{\alpha3}$-C_{m3}	1.414	1.413	1.410	1.411
$C_{\alpha4}$-C_{m3}	1.407	1.411	1.410	1.412
$C'_{\alpha4}$-C_{m4}	1.420	1.425	1.416	1.422
$C_{\alpha1}$-C_{m4}	1.409	1.408	1.400	1.402

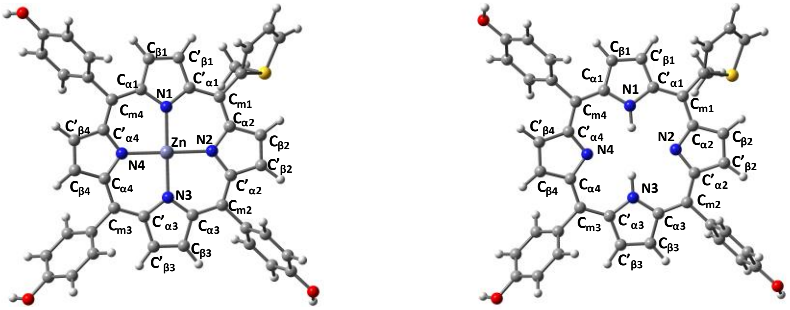
Table S2: Total energies (T.E.) and singlet-triplet energy gap (ΔE) of different compounds.

Compound	Electronic State	T. E. (a.u.)	ΔE (ev)
T2(OH)2MZn	^1A	-4562.95543466	1.234
	^3A	-4562.91010297	
T2(OH)2M	^1A	-2784.92052033	1.079
	^3A	-2784.88086795	
T(OH)3MZn	^1A	-4277.84213682	1.082
	^3A	-4277.80236862	
T(OH)3M	^1A	-2499.80833582	1.003
	^3A	-2499.77149015	

Figure S1: Optimized molecular structures of the target *photosensitizers*.



(1) **T2(OH)2MZn** *(2)* **T2(OH)2**



(3) **T(OH)3MZn** *(4)* **T(OH)3M**

Figure S2: Overlaid absorption spectra of the target photosensitizers T2(OH)2M and T2(OH)2MZn recorded in water (at 10 μM concentration) at 90 days interval.

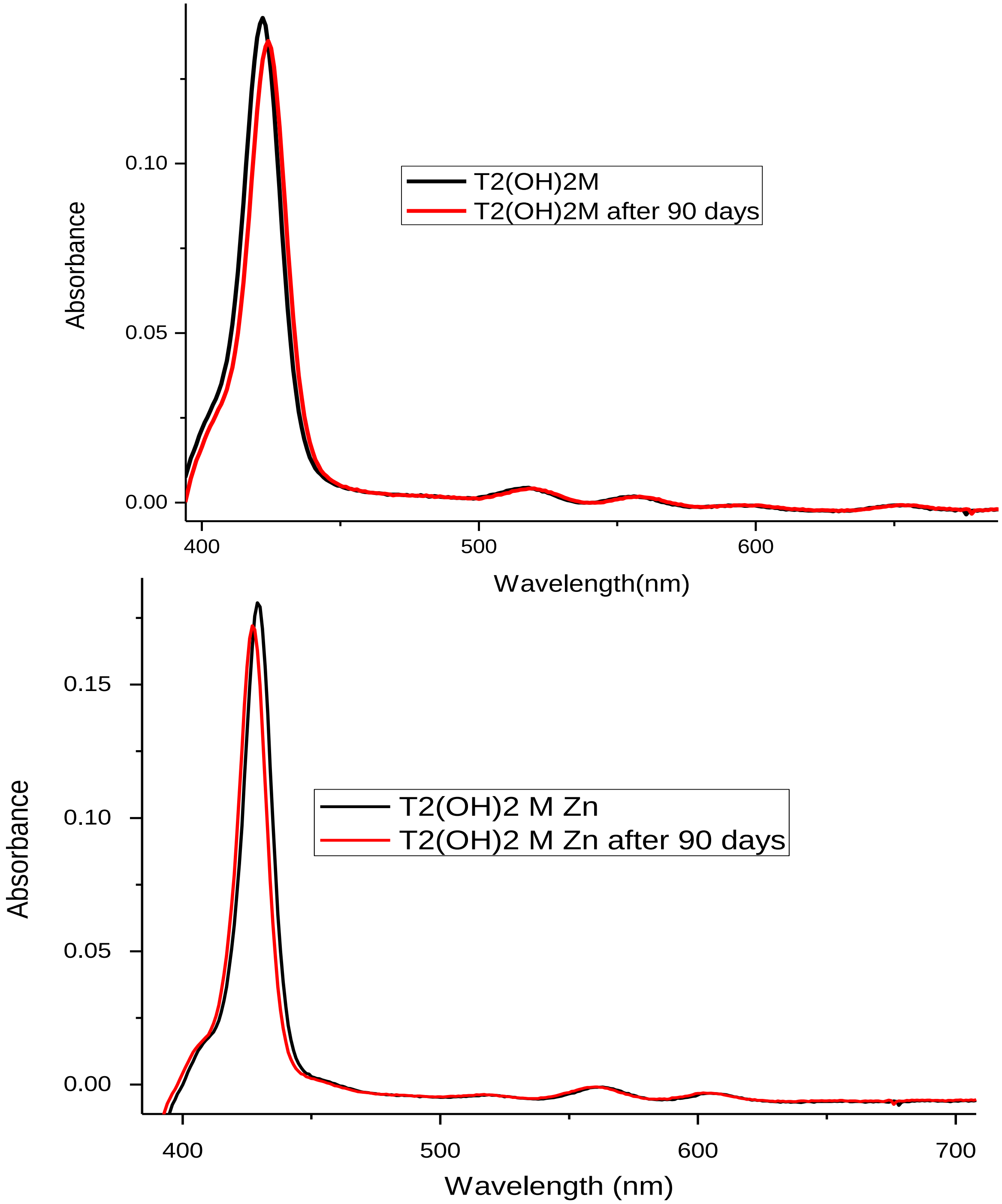


Figure S3: Overlaid absorption spectra of the target photosensitizers T(OH)3M and T(OH)3MZn recorded in water (at 10 μM concentration) at 90 days interval.