Electronic Supplementary Information

Increasing the efficiency of zinc-phthalocyanine based solar cells through modification of the anchoring ligand.[#]

Miguel García-Iglesias,[a] Juan-José Cid,[a] Jun-Ho Yum,[b] Amparo Forneli,[c] Purificación Vázquez,[a] Mohammad K. Nazeeruddin[b]* Emilio Palomares,[c,d]* Michael Grätzel,[b] and Tomas Torres[a,e]*

[a] *Universidad Autónoma de Madrid, Departamento de Química Orgánica, Cantoblanco, 28049-Madrid, Spain.*
[b] *Laboratory for Photonics and Interfaces, Institute of Chemical Sciences and Engineering, School of Basic Sciences, Swiss Federal Institute of Technology, CH-1015 Lausanne (Switzerland).*
[c] *Institute of Chemical Research of Catalonia (ICIQ), Lab 1. Avda. Països Calatans, 16. 43007. Tarragona. Spain.*
.[d] *ICREA. Passeig Lluís Companys, 23. 08010. Barcelona. Spain.*
[e] *IMDEA-Nanociencia. Facultad de Ciencias, Cantoblanco, 28049- Madrid, Spain*

E-mail: tomas.torres@uam.es; mdkhaja.nazeeruddin@epfl.ch; emilio.palomares@iciq.es

Dedicated to the Memory of Professor José Manuel Concellón Gracia

Index *Page*

EXPERIMENTAL DETAILS

Chemicals employed all over this work were purchased from Aldrich Chemical Co. and used as received without further purification. Dry solvents were purchased from SDS in *anhydrous grade* and dried in addition, over molecular sieves (4Å size) acquired from SDS, as well. Prior to use the molecular sieves were dried in an oven during one night and subsequently activated by microwave oven-assisted irradiations took it in turns with a vacuum pump system. The monitoring of the reactions was carried out by TLC, employing aluminum sheets coated with silica gel 60 F_{254} (normal phase) or with LiChroprep RP-18 $F_{254\text{-}S}$ (reverse phase), both purchased from Merk.

Purification of compounds was performed by flash column chromatography using silica gel Merck-60 (230-400 mesh, 0.040-0.063 mm) or Merck LiChroprep RP-18 $F_{254\text{-}S}$ (25-40 μm) for reverse phase. Organic eluants were purchased from SDS in a *synthesis grade*, while water for reverse phase was used in a *milli-Q grade*.

Melting points were determined in a Büchi 504392-S equipment and are uncorrected. NMR spectra were recorded with BRUKER AC-300 and 500 instruments. Deuterated solvent employed is indicated in brackets for each case. Chemical shift values (δ) are referred to tetramethylsilane (TMS), utilized as internal reference. UV/Vis. spectra were recorded in solution using solvents purchased from Fluka Chemie in s*pectroscopic grade* on a Hewlett-Packard 8453 spectrophotometer. The logarithm of the absortion coefficient (ε) is indicated in brackets for each maximum. FT-IR spectra were recorded on a Bruker Vector 22 spectrophotometer, employing for all cases, solid samples embedded in pressed disks of KBr. MS (Matrix-Assisted Laser Desorption Ionization Time-Of-Flight) and HR-MS were performed in a REFLEX-III apparatus with a laser beam operating at 337 nm. Dithranol (1,8,9-anthracenetriol) and PEGNa1000 poly(ethylenglycol)-1000 were used as matrix and internal reference, respectively. Elemental Analyses were performed with a Perkin Elmer 2400 CHN analyzer.

Synthesis of phthalocyanines TT6, TT7, TT8 TT15 and TT16

3-[(Zinc(II) 9(10), 16(17), 23(24)-tri-*tert*-butylphthalocyanyl)]acrylic acid (mixture of regioisomers) TT6

To a vigorously stirred solution of aldehyde **1** (100mg, 0.12 mmol) in acetone (68 mL) cooled to 0 ºC $NaClO_2$ (33.7 mg, 0.36 mmol) was added in a few portions. Afterwards, a solution of sulfamic acid (36.6 mg, 0.36 mmol) in Milli-Q grade deionized water (8.6 mL) was added in one portion, and the reaction mixture was allowed to proceed at RT for 4 h. At the end of the reaction, the mixture was poured into aqueous HCl solution (0.1 M, 300 mL) and a blue-greenish solid precipitated. The solid was filtered over Celite and washed with H_2O and mixtures of H_2O/MeOH (3:1 and 2:1, 100 mL each). Then was dried under vacuum and extracted with THF. The solvent was evaporated and the residue was triturated in hexane, filtered, and washed with a solution of H_2O/MeOH (1:1, 50 mL) and finally with cold MeOH (25 mL) to afford a dark green solid. Further purification could be accomplished by column chromatography (reverse phase, H_2O/THF 1:2) to yield 42 mg (43 %) of **TT6**. Mp: > 250 ºC; ^{1}H-NMR (300 MHz, [D_6]DMSO, 25 ºC, TMS): δ9.62-8.90 (m, 8H, PcH), 8.66-8.38 (m, 4H, PcH), 7.40-7.29 (m, 2H, Pc$\underline{CH}$=C$\underline{H}$$CO_2H$)1.9-1.66 (s, 27H, $C(CH_3)_3$) ppm; FT-IR (KBr): ν 3398, 2951, 2897, 1686, 1632, 1491, 1396, 1329, 1261, 1180, 1086, 982, 918, 825, 750, 673, 544 cm^{-1}; UV/Vis (THF): λ_{max} (log ε) 688 (5.18), 674 (5.15), 613 (4.49), 3.54 (4.87) nm; MS (MALDI-TOF, dithranol): *m/z* 821-814.3 $[M]^+$, (100%); HR MALDI-TOF MS, dithranol: *m/z* 814.27161 [M^+], calcd for $C_{47}H_{42}N_8O_2Zn$: 814.27222.

General procedure for phthalocyanines via cyanoacetic acid or malonic acid: TT7, TT8 and TT15, and TT16.

A solution of formyl phthalocyanines **2** or **1** (0.12 mmol), cyanoacetic acid (59.4 mg, 0.6 mmol) or malonic acid (62 mg, 0.6 mmol) and piperidine (0.28mL, 2.88 mmol) in methanol (10 mL) was heated to reflux under argon atmosphere for 4h. The reaction mixture was then cooled to RT and concentrated under vacuum. The solid residue was extracted with THF, washed with brine, and acidified until pH < 3 with H_3PO_4. After removal of the solvent at reduced pressure, the crude obtained was purified by column chromatography (reverse phase, THF/water 2:1). The solution was extracted with THF and washed with brine. Then THF was removed under vacuum and the solid obtained was triturated in hexane and washed with water and mixtures of H_2O/MeOH (3:1 and 2:1, 100 mL each) affording carboxyphthalocyanines **TT7** (54%), **TT8** (47%) derived from cyanoacetic acid, and **TT15** (60%) **TT16** (52%) derived from malonic acid, respectively.

(*E*)-2-Cyano-3-[(zinc(II) 9(10), 16(17), 23(24) tri-*tert*-butylphthalocyaninyl)]acrylic acid (mixture of regioisomers) TT7

M.p.: > 250 ºC; ^{1}H-NMR (300 MHz, [D$_6$]DMSO, 25º C, TMS): δ 9.41-8.69 (m, 10H, PcH), 8.48-8.21 (m, 3H, PcH, $\mathrm{Pc\underline{CH}{=}CCNCO_2H}$), 2.0-1.8 (s, 27H,$\mathrm{C(CH_3)_3}$); FT-IR (KBr): ν 3410, 2961, 2214, 1610, 1491, 1396, 1342, 1261, 1153, 1086, 922, 837, 744, 690, 602, 484 cm^{-1}; UV/Vis (THF): λ_{max} (log ε) 701 (5.2), 671 (5.3), 610 (4.6), 357 (5.1) nm; MS (MALDI-TOF, dithranol): *m/z* 846-839 [M]$^+$ (100%); HR MALDI-TOF MS, dithranol: *m/z* 839.26709 [M$^+$], calcd for $\mathrm{C_{48}H_{41}N_9O_2Zn}$: 839.26747.

(2*E*, 4*E*)-2-Cyano-5-[(zinc(II) 9(10), 16(17), 23(24) tri-*tert*-butylphthalocyaninyl)]penta-2,4-dienoic acid (mixture of regioisomers) TT8

M.p.: > 250 ºC; ^{1}H-NMR (300 MHz, [D$_6$]DMSO, 25º C, TMS): δ 9.37-8.69 (m, 8H, PcH), 8.54-8.13 (m, 5H, PcH, $\mathrm{PcCH{=}CH\text{-}\underline{CH}{=}CCNCO_2H}$), 8.10-7.93 (m, 1H, $\mathrm{PcCH{=}\underline{CH}\text{-}CH{=}CCNCO_2H}$), 7.83-7.62 (m, 1H, $\mathrm{Pc\underline{CH}{=}CH\text{-}CH{=}CCNCO_2H}$), 2.03-1.78 (s, 27H, $\mathrm{C(CH_3)_3}$); FT-IR (KBr): ν 3356, 2951, 2224, 1612, 1491, 1383, 1329, 1261, 1180, 1113, 1086, 924, 829, 748, 681, 532 cm^{-1}; UV/Vis (THF): λ_{max} (log ε) 704 (5.1), 674 (5.1), 614 (4.4), 358 (4.9) nm; MS (MALDI-TOF, dithranol): *m/z* 872-865 [M]$^+$ (100%); HR MALDI-TOF MS, dithranol: *m/z* = 865.28265 [M$^+$], calcd for $\mathrm{C_{50}H_{43}N_9O_2Zn}$: 865.28312.

2-[(Zinc(II) 9(10), 16(17), 23(24) tri-*tert*-butylphthalocyaninylmethylen]malonic acid (mixture of regioisomers) TT15

M.p.: > 250 ºC; ^{1}H-NMR (300 MHz, [D$_6$]DMSO, 25º C, TMS): δ 9.62-9.09 (m, 8H, PcH), 8.62-8.30 (m, 5H, PcH, $\mathrm{Pc\underline{CH}{=}C(CO_2H)_2}$), 2.1-1.8 (s, 27H, $\mathrm{C(CH_3)_3}$); FT-IR (KBr): ν 3396, 2964, 1664, 1678, 1610, 1489, 1394, 1327, 1286, 1259, 1151, 1084, 1043, 922, 827, 746, 692, 611 cm^{-1}; UV/Vis (THF): λ_{max} (log ε) 677 (5.2), 612 (4.5), 353 (4.7) nm; MS (MALDI-TOF, dithranol): *m/z* 865-858 [M]$^+$ (100%); HR MALDI-TOF MS, dithranol: *m/z* 858.26190 [M$^+$], calcd for $\mathrm{C_{48}H_{42}N_8O_4Zn}$: 858.26205.

2-[(*E*)-3-(Zinc(II) 9(10), 16(17), 23(24) tri-*tert*-butylphthalocyaninyl)allyldien]malonic acid (mixture of regioisomers) TT16

M.p.: > 250 ºC; ^{1}H-NMR (300 MHz, [D$_6$]DMSO, 25º C, TMS): δ 9.5-9.18 (m, 8H, PcH), 9.0-8.86 (m, 1H, PcCH=CH-$\underline{\text{CH}}$=C(CO$_2$H)$_2$), 8.5-8.33 (m, 4H, PcH), 8.15-7.98 (d, 1H ^3J=15.2Hz, PcCH=$\underline{\text{CH}}$-CH=C(CO$_2$H)$_2$), 7,94-7.84 (d, 1H ^3J=15.2Hz, Pc$\underline{\text{CH}}$=CH-CH=C(CO$_2$H)$_2$), 1.92-1.84 (s, 27H; C(CH$_3$)$_3$); FT-IR (KBr): ν 3402, 2930, 2916, 2849, 1643, 1616, 1468, 1373, 1319, 1252, 1090, 1049, 901, 829, 743, 640, 613 cm^{-1}; UV/Vis (THF): λ_{max} (log ε) 692 (5.1), 677 (5.0), 617 (4.4), 354 (4.9) nm; MS (MALDI-TOF, dithranol): *m/z* 891-884 [M]$^+$ (100%); HR MALDI-TOF MS, dithranol: *m/z* 884.27893 [M$^+$], calcd for $C_{50}H_{44}N_8O_4Zn$: 884.27777.

Optical measurements, Electron Recombination Measurements, Electron Injection Measurements, Electrochemical measurements and Dye Sensitized Solar Cells

UV-Visible and emission fluorescence measurements. The UV-Visible spectra of all the phthalocyanine dyes in tetrahydrofuran solvent (HPLC degree) were recorded in a Shimadzu© UV-Visible system model 1700. The dyes fluorescence emission properties, either in solution or adsorbed onto the metal oxide films, were measured under ambient conditions using an Aminco Bowman Series 2 luminescence spectrometer equipped with a temperature controller and a holder for films and solid samples.

Nanocrystalline TiO_2 and Al_2O_3 films for optical measurements. The metal oxide nanoparticles were sensitized as reported previously[16]. In brief, Al_2O_3 nanoparticles were purchased from Alfa-Aesar chemical (20% in H_2O, colloidal dispersion) and 15 mL of the colloidal dispersion were mixed with 0.35g of hydroxypropyl cellulose (2 wt% of Al_2O_3). The mixture was stirred for 7 days at 65ºC. For the TiO_2 colloids we followed previous literature reports[16]. In order to prepare the transparent mesoporous metal oxide films, transparent glass cover slides were cleaned and a drop of the corresponding metal oxide paste was spread using a glass rod. After drying the films in air, the films were calcined at 450^0C for 30 minutes. The measured thickness was 4µm.

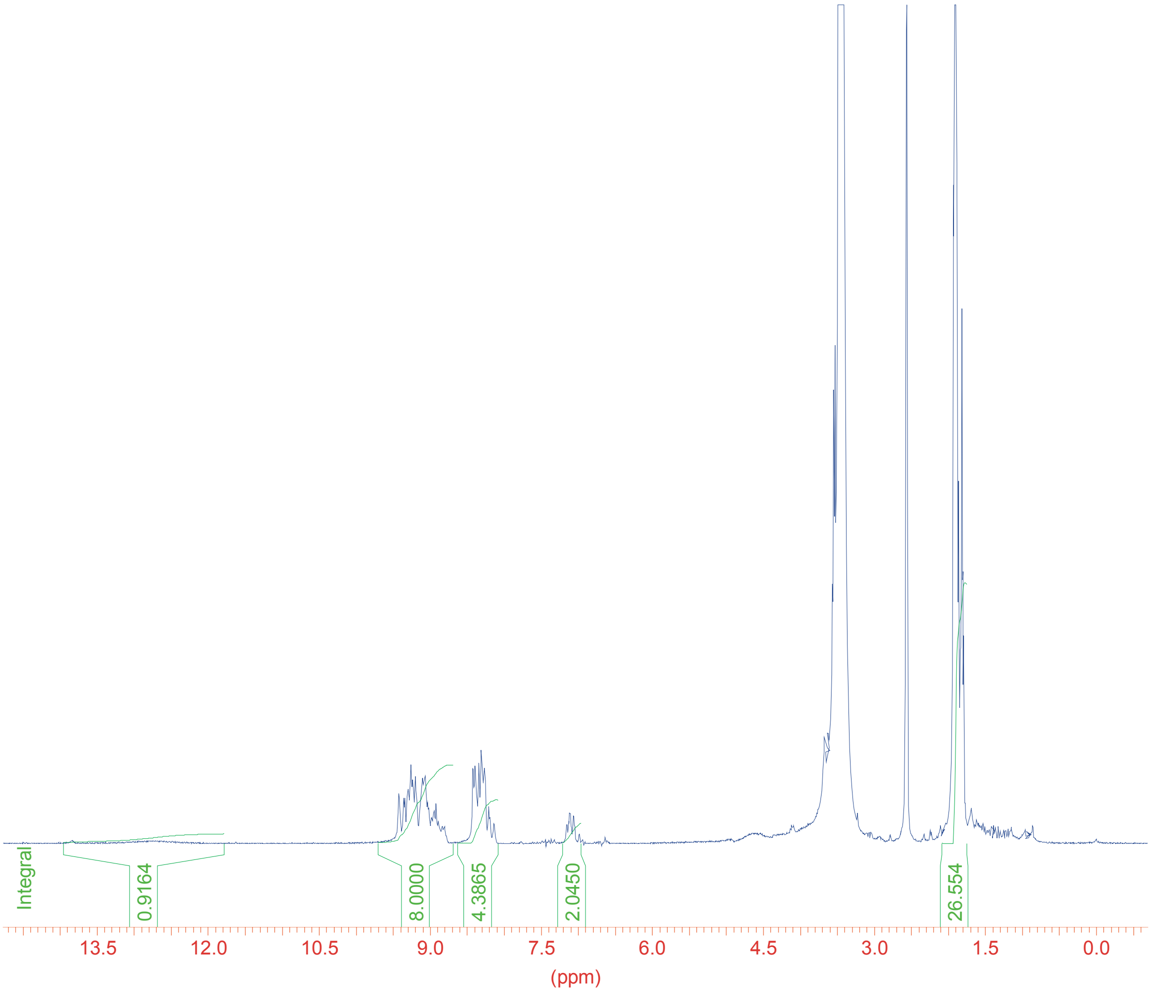
Electron Recombination Measurements. Laser transient absorption spectroscopy was used to determine the recombination lifetime of the phthalocyanine sensitized TiO_2 films. All the films had the same absorbance value. The experiments were carried out as reported before. Briefly, a PTI Nitrogen Dye Laser model was used as excitation source with the appropriated dye solution. The laser power was kept constant during the experiment to 0.05 mJ/cm^2 with a repetition rate of 1 Hz (pulse duration less than 1 nanosecond). The resulting photo-induced change in optical density was monitored employing a 150W Tungsten Lamp, with 20 nm bandwidth PTI monochromators before and after the sample, a photodiode based detection system from Costronic Electronics© and a TDS-220 Tecktronic© DSO oscilloscope.

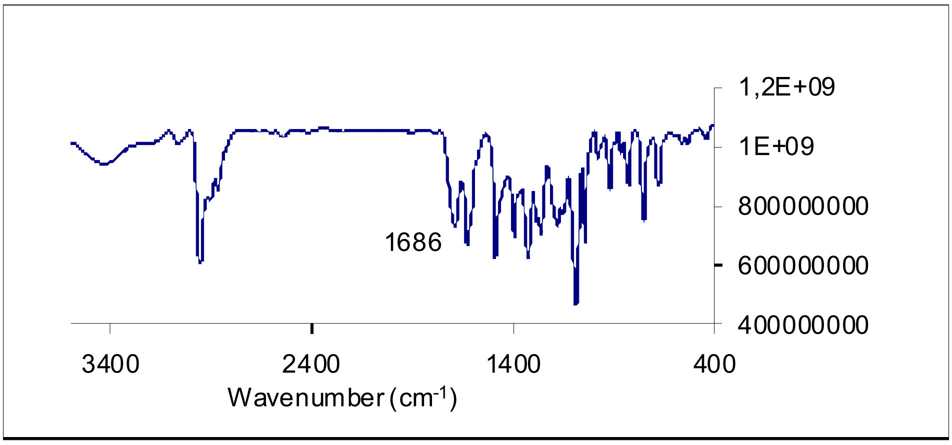
Electron Injection Measurements. Time Correlated Single Photon Counting measurements of complete DSSC devices were carried out using an Edinburgh Instruments© system model LifeSpec-PS. As excitation source we used a picosecond laser diode λ_{ex} = 635 nm (laser power 2 nJ/cm^2 by pulse) with an instrument response of 325 ps FWHM (Full Width at Half Maximum). As control samples we utilized Al_2O_3 sensitized films with identical absorbance at the excitation wavelength. The high conduction band of Al_2O_3 prevents the electron injection from the dye-excited state. The calculation of the injection yield is done by comparison of the area under the signal area of the control and the sample.

Electrochemical measurements: Measurements were done by cyclic voltammetry in a conventional thee-electrode cell connected to a CH Instruments 660c potentiostat-galvanostat. We used tetrabutyl ammonium perchlorate (TBAP) as electrolyte, a platinum working electrode, a calomelan reference electrode (SCE) and a platinum wire as auxiliary electrode. The 0.5×10^{-4} M solutions in THF were purged with Ar during 5 minutes prior to measurements.

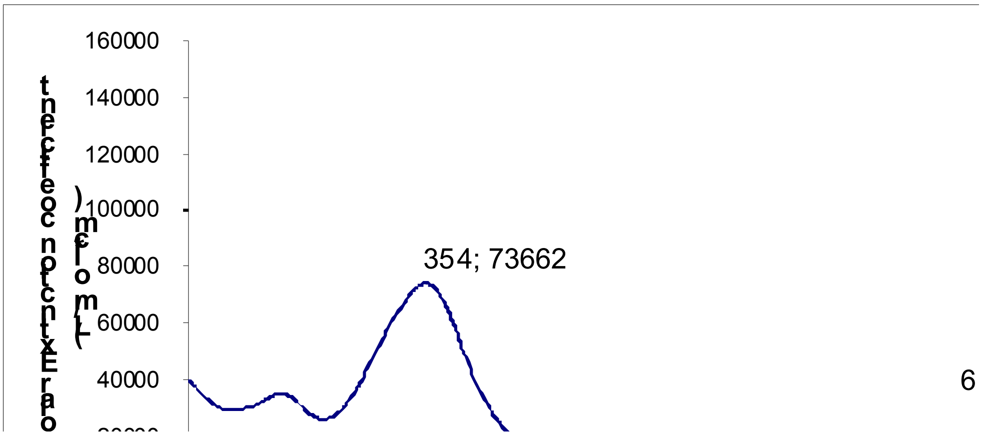
Dye Sensitized Solar Cells: The screen-printed double layer film of TiO_2 consists of a 9 ~ 10 µm transparent layer and a 4 µm scattering layer and were prepared and treated with 0.05 M titanium tetrachloride solution using a previously reported procedure. The film was heated to 500 ºC in air and calcined for 20 min before use. Dye solutions were prepared in the concentration range of $0.5 - 1 \times 10^{-4}$ M solution in ethanol containing (10 – 60 mM) 3a,7a-dihydroxy-5b-cholanic acid (Cheno). The electrodes were dipped into the dye solution for 4 hours at 22°C and the dye-coated electrodes were rinsed quickly with ethanol and used as such for photovoltaic measurements. The electrolyte was composed of (0.6M M-methyl-N-butyl imidiazolium iodide, 0.04 M iodine, 0.025 M LiI, 0.05M guanidinium thiocyanate and 0.28 M tertiary butylpyridine in 15/85 (v/v) mixture of valeronitrile and acetonitrile. The dye-adsorbed TiO_2 electrode and thermally platinized counter electrode were assembled into a sealed sandwich type cell with a gap of a hot-melt ionomer film (Surlyn 1702, 25 µm thickness, Du-Pont). In order to reduce scattered light from the edge of the glass electrodes of the dyed TiO2 layer, a light-shading mask was used onto the DSSCs, so active area was fixed to 0.2 cm^2. For photovoltaic measurements of the DSSCs, the irradiation source was a 450 W xenon light source (Osram XBO 450, USA) using a Tempax 113 solar filter (Schott). The output power of an AM 1.5 solar simulator was calibrated by using a reference Si photodiode equipped with a colored matched IR-cutoff filter (KG-3, Schott) in order to reduce the mismatch in the region of 350-750 nm between the simulated light and AM 1.5 to less than 4%. The measurement delay time of photo I-V characteristics of DSSCs was fixed to 40 ms. The measurement of incident photon-to-current conversion efficiency (IPCE) was plotted as a function of excitation wavelength by using the incident light from a 300 W xenon lamp (ILC Technology, USA), which was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd.).

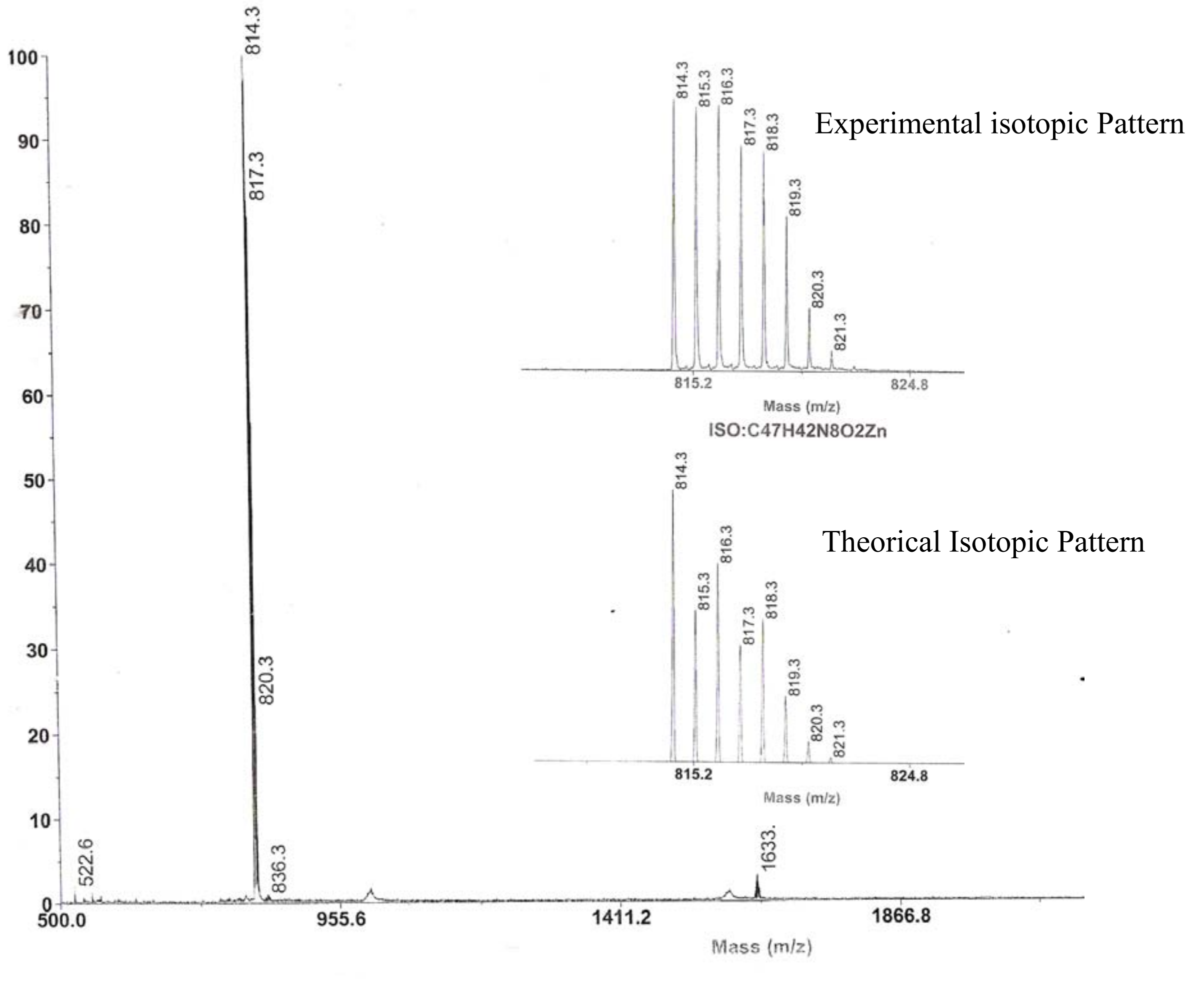
^{1}H-NMR and FT-IR spectra of phthalocyanine TT6



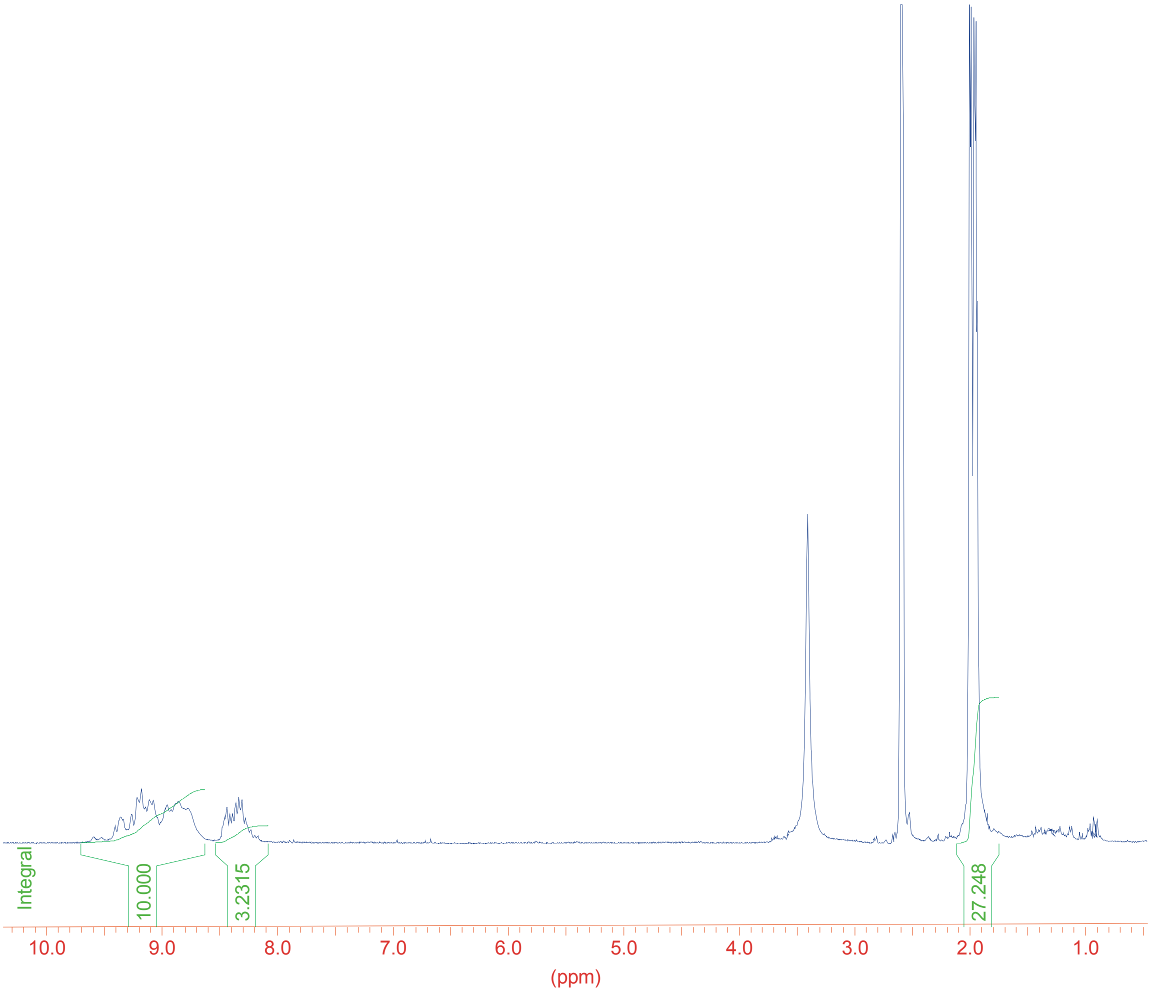


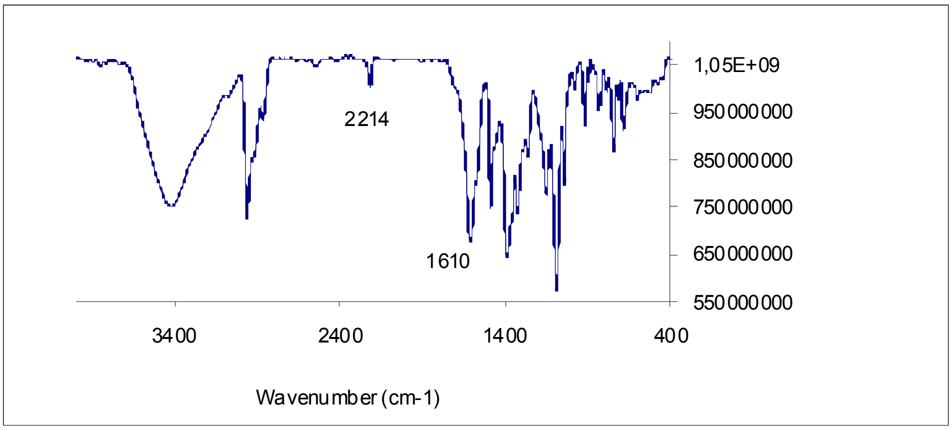
UV-Vis. and MALDI-TOF spectra and isotopic distribution pattern (inset) of phthalocyanine TT6



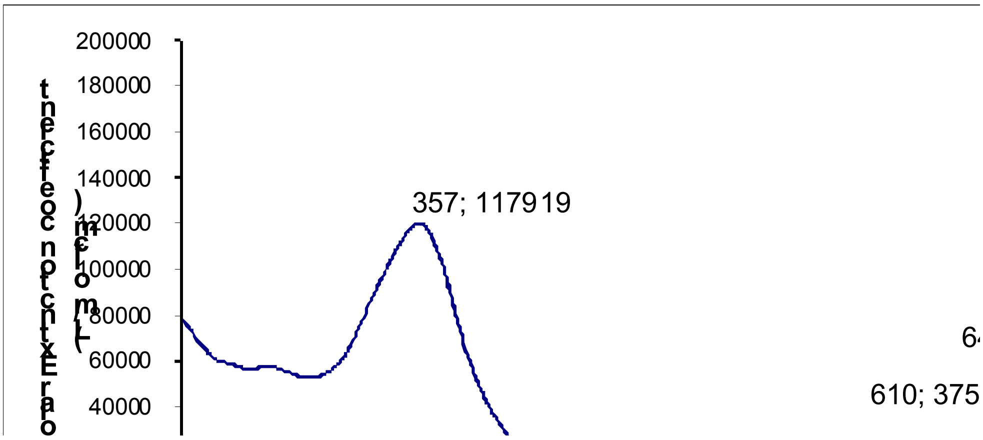


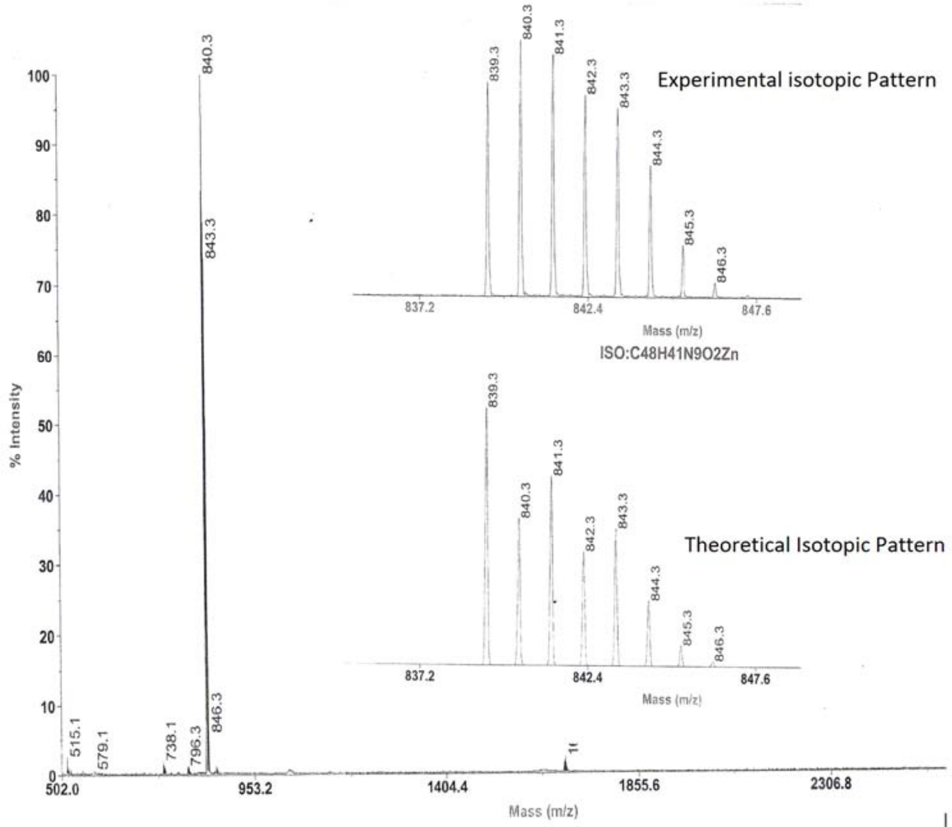
^{1}H-NMR and FT-IR spectra of phthalocyanine TT7



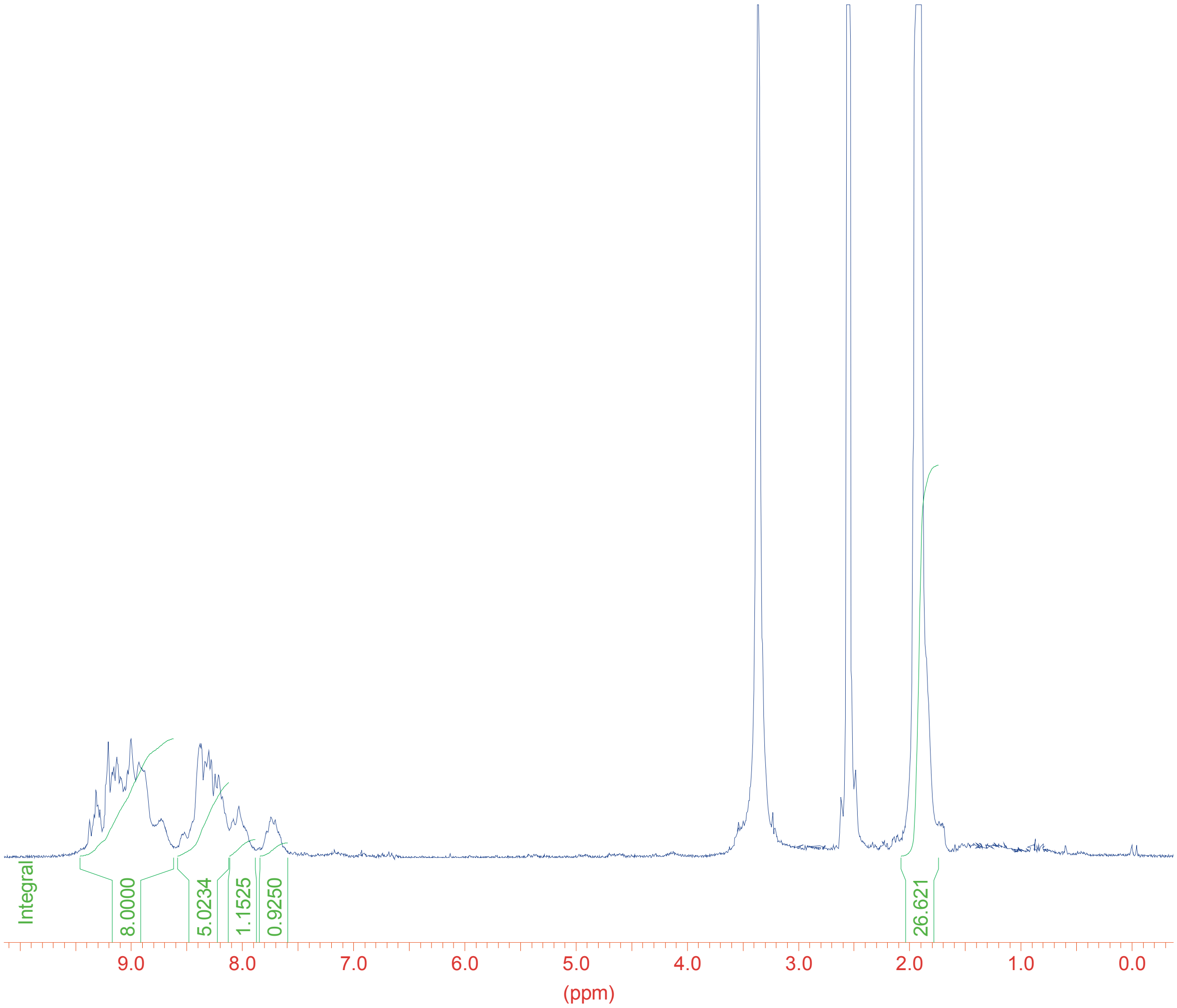


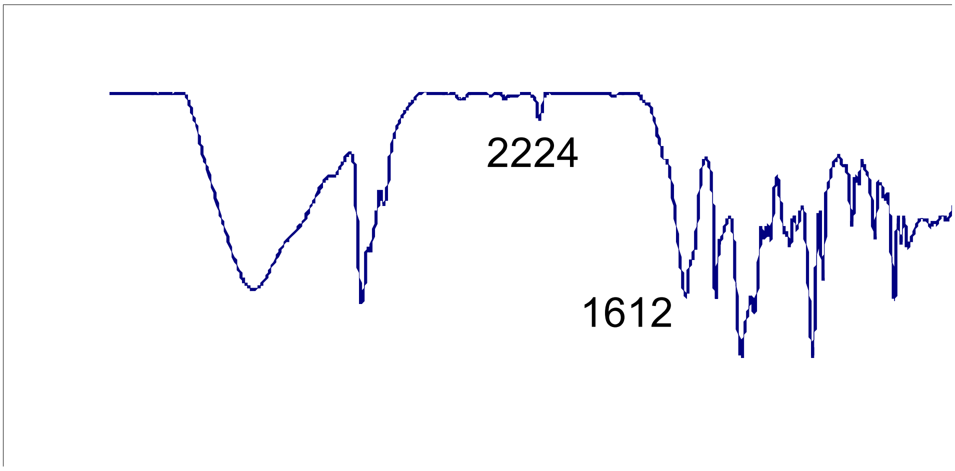
UV-Vis. and MALDI-TOF spectra and isotopic distribution pattern (inset) of phthalocyanine TT7



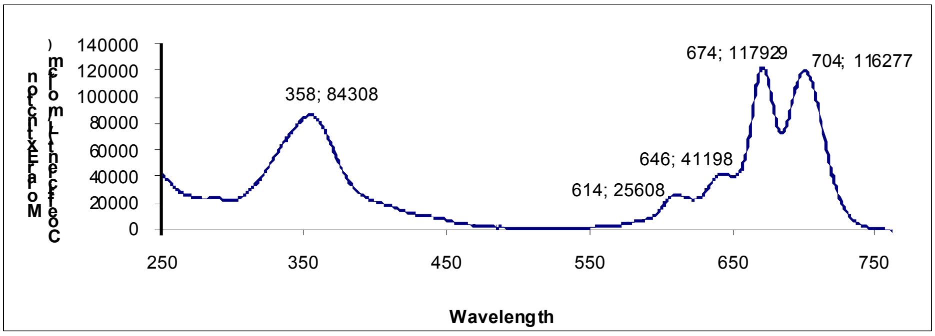


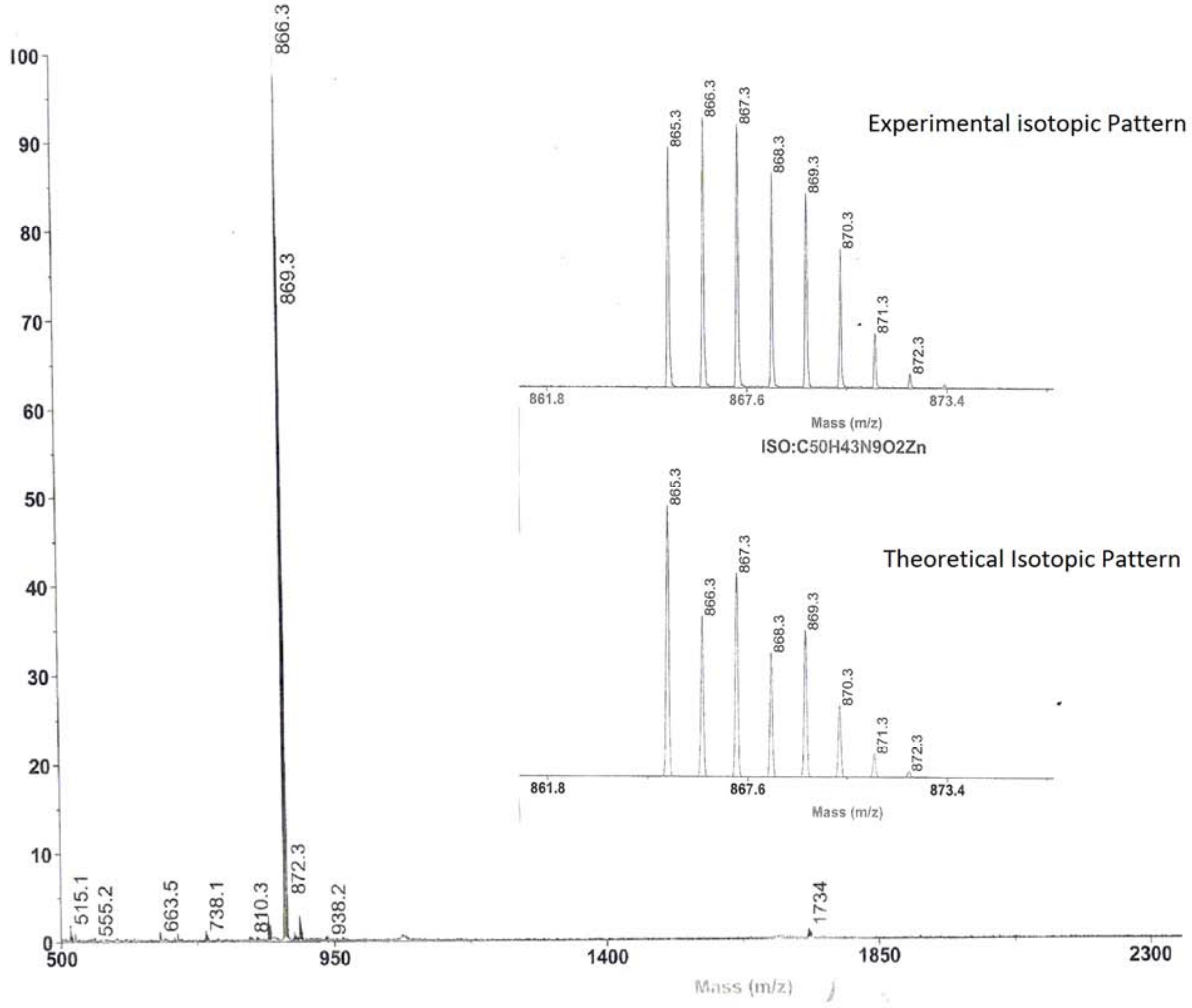
^{1}H-NMR and FT-IR spectra of phthalocyanine TT8



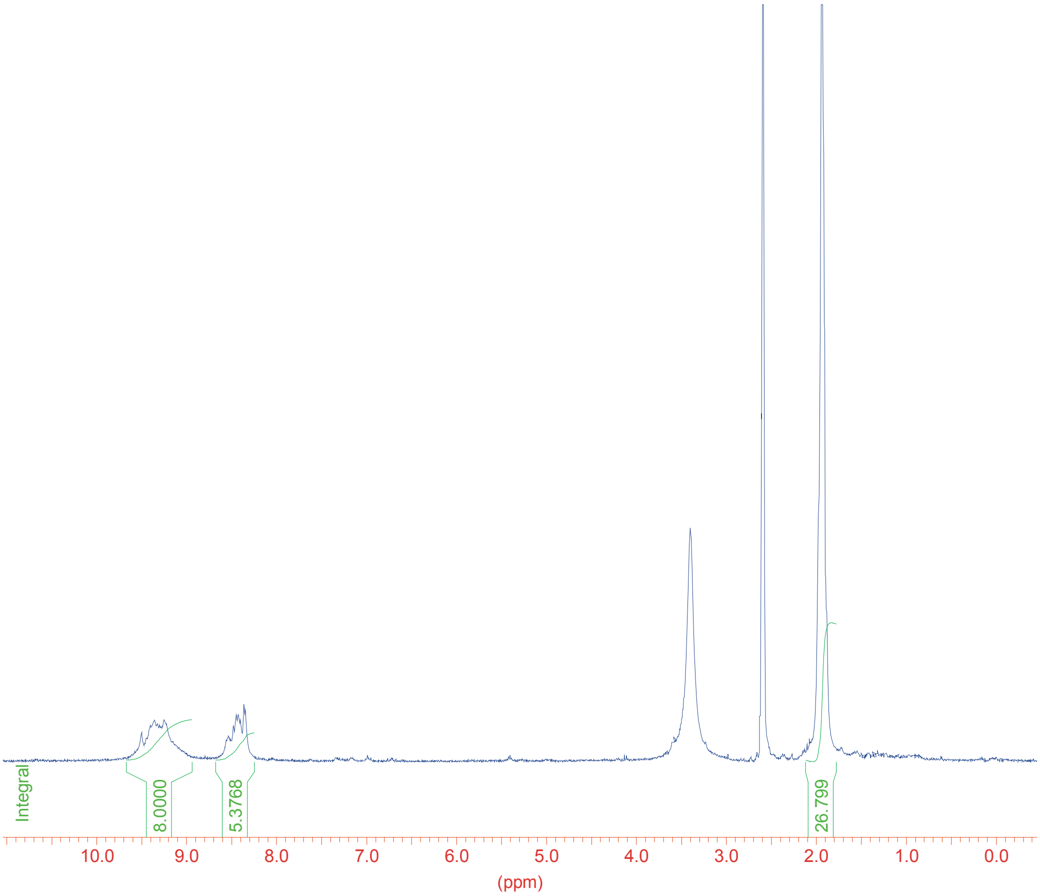


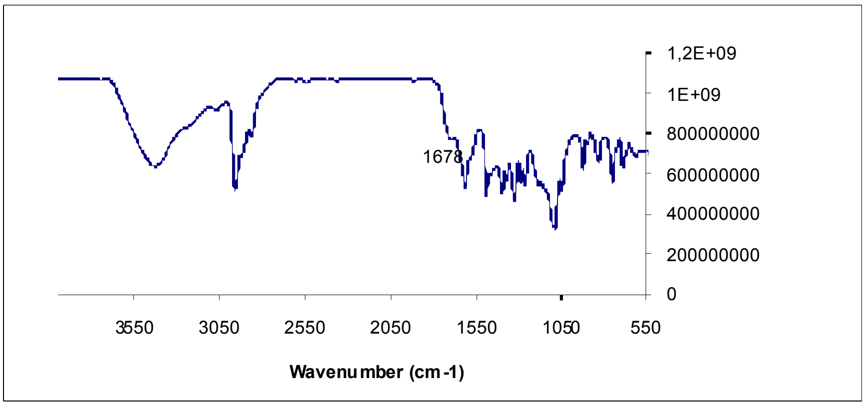
UV-Vis. and MALDI-TOF spectra and isotopic distribution pattern (inset) of phthalocyanine TT8



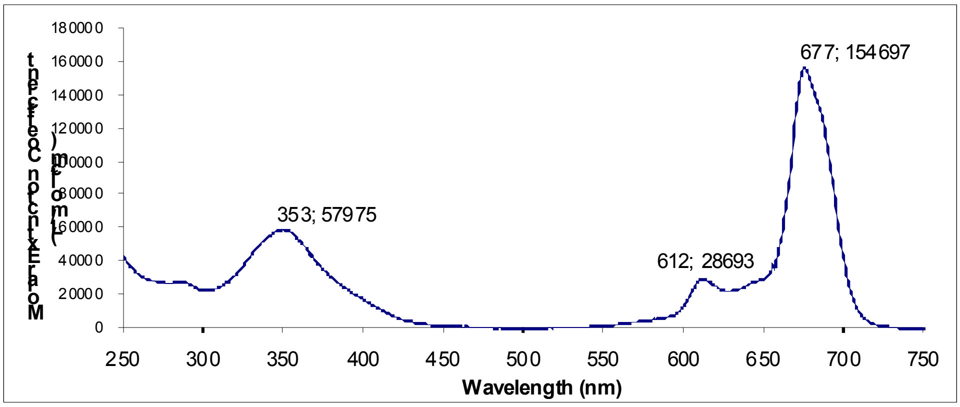


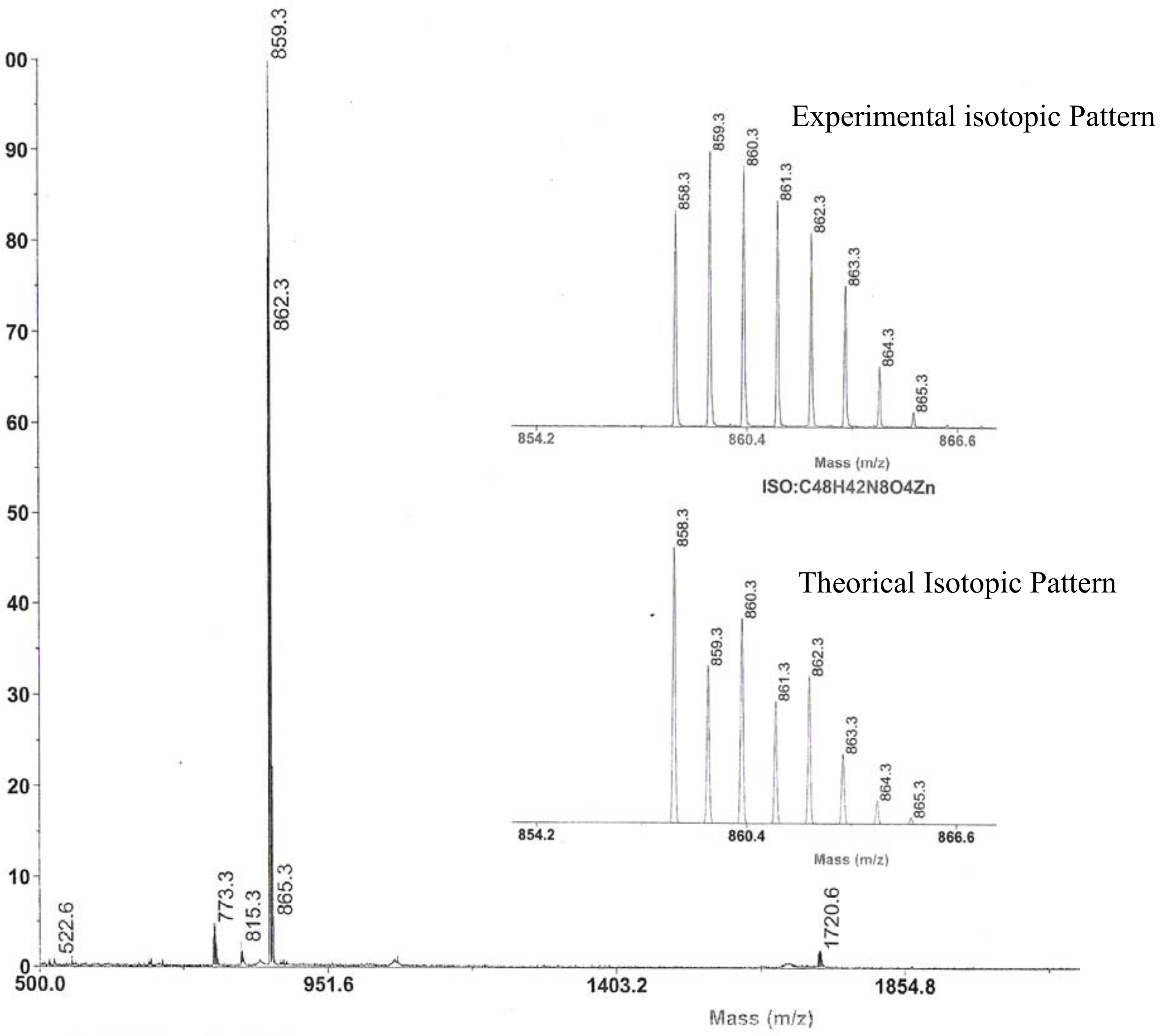
^{1}H-NMR and FT-IR spectra of phthalocyanine TT15



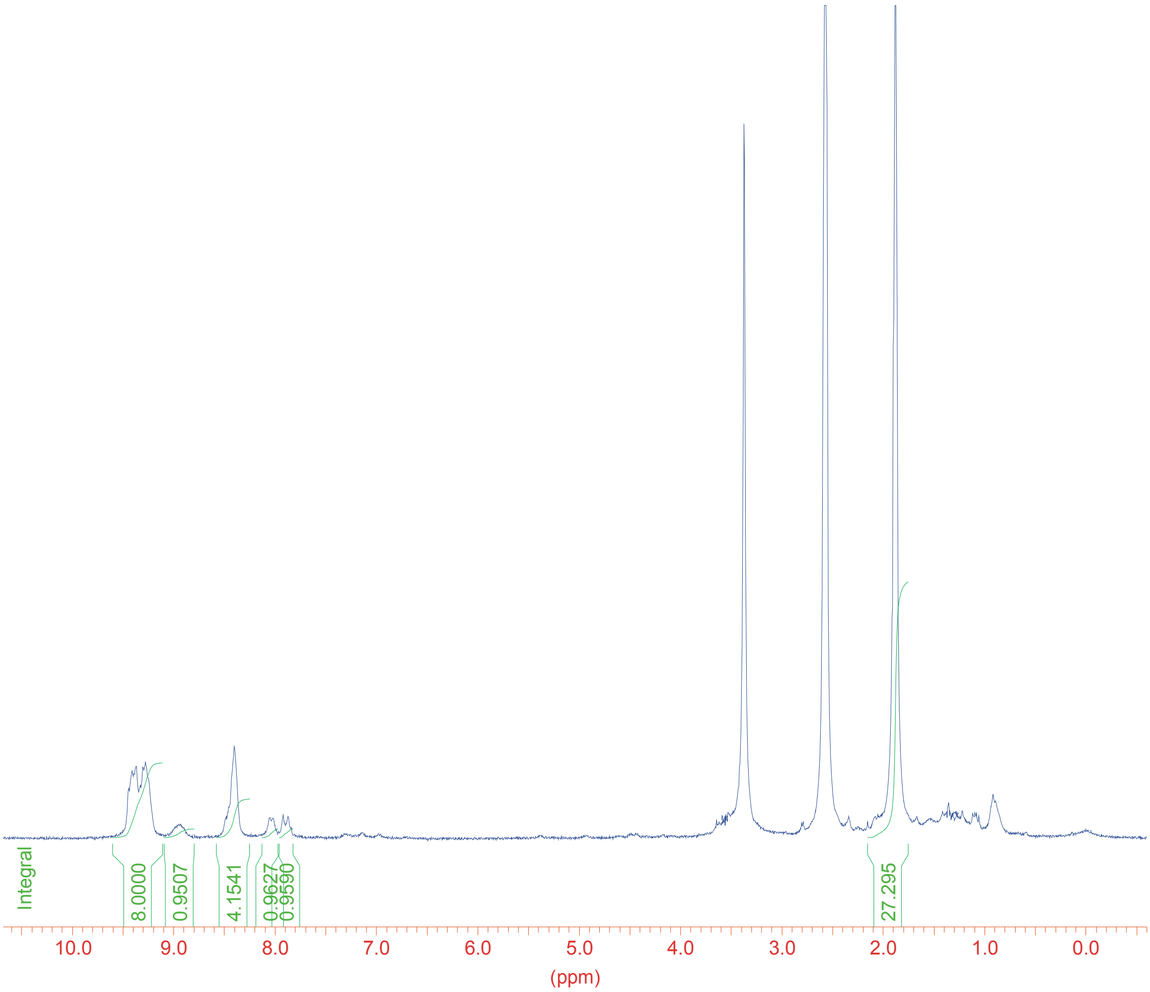


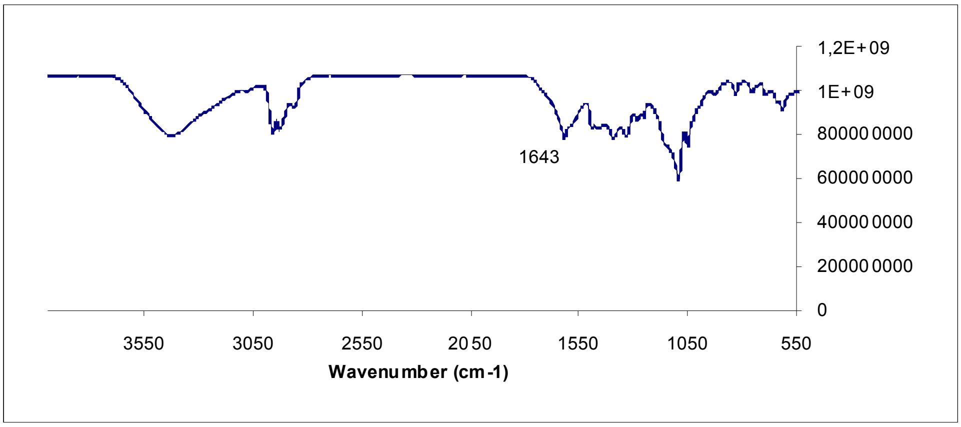
UV-Vis. and MALDI-TOF spectra and isotopic distribution pattern (inset) of phthalocyanine TT15





^{1}H-NMR and FT-IR spectra of phthalocyanine TT16





UV-Vis. and MALDI-TOF spectra and isotopic distribution pattern (inset) of phthalocyanine TT16