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# Photodynamic antimicrobial activities and laser flash photolysis studies of meso-tetrakis (2-bromophenyl), meso-tetrakis (3-bromophenyl) and meso-tetrakis (4-bromophenyl) tin porphyrins

## [Activités antimicrobiennes photodynamiques et études de photolyse laser éclair des porphyrines d'étain méso-tétrakis (2-bromophényl), méso-tétrakis (3-bromophényl) et méso-tétrakis (4-bromophényl)]

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**Abstract**

The photodynamic antimicrobial activities and laser flash photolysis studies were conducted for meso-tetrakis (2-bromophenyl), meso-tetrakis (3-bromophenyl) and meso-tetrakis (4-bromophenyl) free base porphyrins and their Sn(IV) complexes. It has been shown that Tin Metalated porphyrins have high singlet oxygen quantum yields compare to their respective free bases (0.645, 0.708, 0.732 vs 0.445, 0.585 and 0.412) for 1Sn, 2Sn and 3Sn vs 1, 2 and 3 respectively. The disapearence of *Staphylococcus aureus* or *E. Coli* was observed around 2,5 µM. The decay rate constants of all porphyrins were around 1.50 ×106 s-1 and 2.35 ×104 s-1 for aerated and degassed solutions respectively.

**Keywords**: Laser flash photolysis, free base porphyrins, singlet oxygen quantum yield, photophysics

**Résumé**

Les activités antimicrobiennes photodynamiques et les études de photolyse laser éclair ont été réalisées sur les porphyrines à base libre méso-tétrakis (2-bromophényle), méso-tétrakis (3-bromophényle) et méso-tétrakis (4-bromophényle) ainsi que sur leurs complexes d’étain (IV). Il a été démontré que les porphyrines métallées à l'étain présentent des rendements quantiques d'oxygène singulet élevés par rapport à leurs bases libres respectives (0,645, 0,708 et 0,732 contre 0,445, 0,585 et 0,412 pour 1Sn, 2Sn et 3Sn respectivement). La disparition de *Staphylococcus aureus* ou d'*E. coli* a été observée autour de 2,5 µM. Les constantes de vitesse de décomposition de toutes les porphyrines étaient d'environ 1, 50 × $10^6$ s$^{-1}$ et 2,35 × $10^4$ s$^{-1}$ pour les solutions aérées et dégazées, respectivement.

**Mots-clés:** Photolyse laser éclair, porphyrines à base libre, rendement quantique de l'oxygène singulet, photophysique.

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# 1. Introduction

Antibiotics are mostly used for the treatment of infections such as bronchitis, urinary tract infections, pneumonia, ear infections, meningitis including sexually transmitted diseases that can be caused by bacteria. Nowadays pathogenic bacteria are considered as a serious public health issues because of some resistance observed after the use of common antibiotics (Spellberg, 2008).

In addition, the repeated and excessive use of antibiotics by a human being might be responsible of bacterial resistance to common antibiotics, which can lead to increasingly frequent therapeutic dead ends. In the planktonic forms, pathogenic bacteria can be easily eraducated by using normal dosage compare to when there is a physiological change from floating bacteria cells to biofilms where the higher dosage of antibiotics are tolerated (Donlan, 2002 ; Mirzahosseinipour, 2020). Bacteria such as Staphylococcus Aureus have shown to be resistant against Methicillin and Vancomycin because of their ability to form biofilms which makes difficult the total eraducation(Mamone, 2016).

Among alternative treatment that researchers are currently focused on there is photodynamic antimicrobial chemotherapy (PACT) which combine the synergic use of photosensitizer, light and oxygen (Xu, 2016). This technic which involves the triplet energy transfer has shown some improvement for the treatment of wound infections and dental biofilms (Al-Mutairi, 2018). For the need of the cause photosensitizers used were porphyrin, BODIPY, chlorin, bacteriochlorin and phthalocyanine with light of a specific wavelength in order to generate cytotoxic reactive oxygen species responsible of inactivation or death of cells(Calzavara-Pinton, 2007 ; Saczko, 2008 ; Robertson, 2009).

Previous studies have shown that free porphyrins and their metal complexes especially those containing metals like galium, Zinc etc. have promising antibacterial activities(Openda, 2021 ; Muthumuni, 2018).

The overall goal of this work is to evaluate the photodynamic effects of some porphyrin derivatives on selected gram-positive and gram-negative bacteria and to carry out the nanosecond laser flash photolysis studies of these selected porphyrin derivatives in order to generate different possible intermediates, to know their lifetimes and their transient absorption spectra in aerated and degassed solutions of dichloromethane or methanol. The knowledge of different rate constants and processes undergone while porphyrins are irradiated will allow a complete photophysical studies and a good understanding of the reactivity of the photoreaction.

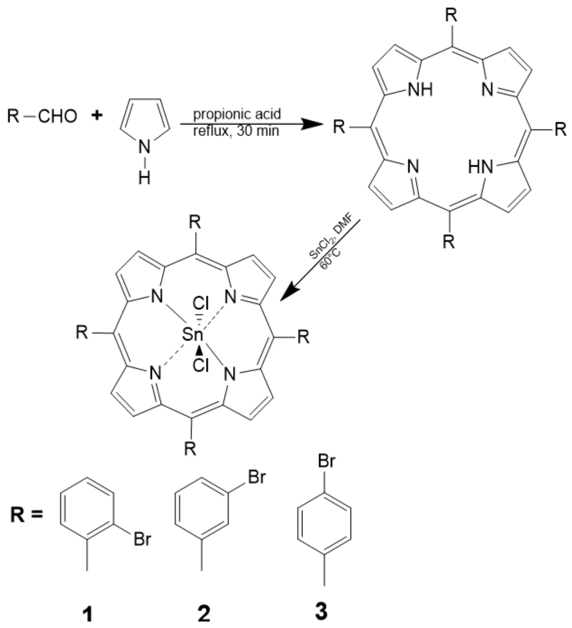


*Figure 1. Synthetic routes of porphyrins.*

# 2. Materials and methods

## 2.1 Materials

2-bromobenzaldehyde, 3-bromobenzaldehyde, 4-bromobenzaldehyde, Propionic acid, Anhydrous Tin (iv) chloride, 9,10-dimethylanthracene (DMA), were purchased from Sigma-Aldrich. Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), Acetonitrile, were purchased from Merck and were used as received. Staphylococcus aureus and Escherichia Coli strains were isolated and identified at the University of Kinshasa Clinics (DRC) and used for antibacterial inactivation studies. The synthesis of metal free meso-tetrakis (2-bromophenyl), meso-tetrakis (3-bromophenyl) and meso-tetrakis (4-bromophenyl) porphyrins was carried out as reported previously with slight modification (Muthumuni, 2018 ; Pereira, 2002)

## 2.2 Equipment

Ground state electronic spectra were taken by a Shimadzu UV-2250 Spectrophotometer and a Brucker AutoFLEX III Smartbeam TOF/TOF mass spectrometer in the positive mode using alpha-cyano-4-hydroxycinnamic acid as a MALDI matrix were used to record mass spectra. The triplet lifetimes ($\tau_T$) were obtained using a laser flash photolysis system made up of an LP 980 spectrometer with a PMT-LP detector and an ICCD camera (Andor DH320T-25F03). Fluorescence emission spectra were recorded on a Varian Eclipse spectrofluorometer with quartz cell of 1 cm at room temperature. 1H NMR spectra were measured in a Varian Inova 400 MHz NMR spectrometer. Light-emitting diode (LED) at 632 nm with an irradiance of 240 mW cm$^{-2}$ was used for sample irradiation.

### *2.3 Laser Flash Photolysis*

The nanosecond laser flash photolysis and transient absorption spectroscopy measurements were performed using an EKSPLA SL334 Nd-YAG laser, with pulses of ≤ 700 ps duration. The output energy at 355 nm excitation was about 175 mJ. In a 1 cm cuvette the absorbance of samples were adjusted between 0.6–0.8 at 355 nm. wavelngths of monitoring kinetic decays were fixed using a photomultiplier and the transient absorption spectra were recorded using an Andor iSTAR incorporated camera. Kinetic traces were obtained by fitting data with flashfit 0.11. Samples were degassed by 3 freeze-thaw cycles under reduced pressure (5 Pa).

### *2.4 Synthesis*

The synthesis of metal free 5, 10, 15, 20-tetrakis (4-bromophenyl) porphyrin has been reported previously in our group following the procedure reported by M. Pereira et al 10,11 as shown in Scheme 1. In a 250 mL two-necked conical flask, the selected aldehyde (1.5.0 g, 10 mmol) was added to a refluxing mixture of propionic acid (100 mL), then freshly distilled pyrrole (2.5 mL, 36 mmol) in 10 mL of propionic acid was added dropwise to the stirring mixture. The reaction mixture was allowed to reflux for 2 hours. The mixture was allowed to cool overnight for efficient precipitation and residue was collected by filtration. The filtrate was washed and dried under vacuum. The tin metallated porphyrins were prepared as reported previously in our group12 were 0.1 equivalent of unmetallated porphyrin and 1 equivalent of tin chloride were dissolved in dry pyridine. The reaction mixture was refluxed for about 2 hours until there was shift B band and collapsed of Q bands in UV spectra from four to two. The mixture was cooled and millipore water was added to precipitate, following by filtration, drying and purification by column chromatographie to yield Tin-porphyrin.

Compound 1. Yield (17 %); FTIR (cm-1): 3300-3450(-NH amine stretch), 2800-3100(C-H Alph. and aro. stretch, CH3-), 1500-1680(C=N and C=C stretches), 1450-1500(C-H and C-N bends). MALDI TOF-MS, calc. 930.34, found 931.29, [M+H] +; UV/visible (CHCl3), ʎmax nm: 418 (Soret band), 517 (QI), 549(QII) 590(QIII) 633 (QIV). 1H NMR (400 MHz, CDCl3) δ 1.23 (t, J = 7.0 Hz, 5H), 1.66 (s, 3H), 2.61 (s, 2H), 2.74 – 3.06 (m, 2H), 3.71 (q, J = 7.0 Hz, 4H), 5.95 (s, 1H), 8.00 (s, 0H), 8.56 (s, 1H).

Compound 2. Yield (20%); FTIR (cm-1): 3300-3450(-NH amine stretch), 2800-3100(C-H Alph. and aro. stretch, CH3-), 1500-1680(C=N and C=C stretches), 1450-1500(C-H and C-N bends). MALDI TOF-MS, calc. 994.33, found 930.3, [M+4OH] +; UV/visible (CHCl3), ʎmax nm: 418 (Soret band), 520 (QI), 552(QII) 584(QIII) 640 (QIV). 1H NMR (400 MHz, CDCl3) 1.23 (4 H, t, J 7.0), 2.70 – 3.27 (2 H, m), 3.71 (2 H, d, J 7.0), 5.95 (1 H, s), 8.01 (0 H, s), 8.56 (1 H, s).

Compound 3. Yield (21%) ; FTIR (cm-1): 3300-3450(-NH amine stretch), 2800-3100(C-H Alph. and aromatique stretch, CH3-), 1500-1680(C=N and C=C stretches), 1450-1500(C-H and C-N bends). MALDI TOF-MS, calc. 932.54, found 930.3, [M+2H] +; UV/visible (CHCl3), ʎmax nm: 420 (Soret band), 517 (QI), 552(QII) 596(QIII) 649 (QIV). 1H NMR (400 MHz, CDCl3) 1.23 (4 H, t, J 7.0), 2.70 – 3.27 (2 H, m), 3.71 (2 H, d, J 7.0), 5.95 (1 H, s), 8.01 (0 H, s), 8.56 (1 H, s).

### *2.5 Antimicrobial studies*

The in vitro antibacterial activity investigations were sorted out using Staphylococcus aureus (Gram +) and Escherichia Coli (Gram –) bacteria collected at the University of Kinshasa Clinics (DRC). The bacteria was prepared individually in nutrient broth (6 mL) and incubated at 37 °C for 18 h while shaking. The optical density (OD) value of the bacteria can be measured for each selected bacteria. Once the OD value range of around 0.6–0.8 the maturation growth was stopped. The bacteria were collected after centrifugation and washed with PBS. The collected bacteria were then diluted in PBS (100 mL) to prepare a bacterial stock suspension with a dilution factor of $10^{-2}$.

The suspension of bacteria with a dilution factor of $10^{-4}$ and around 30–300 CFU/ml prepared from the stock solution was used for these studies.

Optimisation of the concentration were carried out using the porphyrins in 1% DMSO/PBS at 0−100 μM range. 12.5 μM and 25 μM were determined to be the optimal concentration for Staphylococcus aureus and *Escherichia Coli* respectively for further studies. The bacteria (*S. aureus*) solution ($10^{-4}$) and porphyrins (12.5 µM) were used to prepare bacterial-Porphyrins solutions (2.5 mL) and The *E Coli* solution ($10^{-4}$) and porphyrins (25 µM) were used to prepare solutions of bacterial- Porphyrins (2.5 mL)

Solutions were irradiated for 150 min with a 632 nm light dose 77 J/cm$^2$ irradiation using LED or kept in the dark with aliquots for analysis taken at 30 min intervals for 150 min. The dark and irradiated bacterial-Porphyrins solutions (100 µL) were inoculated into nutrient agar at each time interval. The CFU values for the colonies were measured using a 500 Automatic Colony Counter Scan500®.

# 3. Results and discussion

The main goal of this work is to assess and see whether the selected free base and tin metallated porphyrins isomers can be used as photosensitsers in photoantimicrobial applications and to conduct laser flash photolysis in nanosecond scales in order to determine the rate constants transient species along with transient absorption spectra and finally propose the overall mechanism

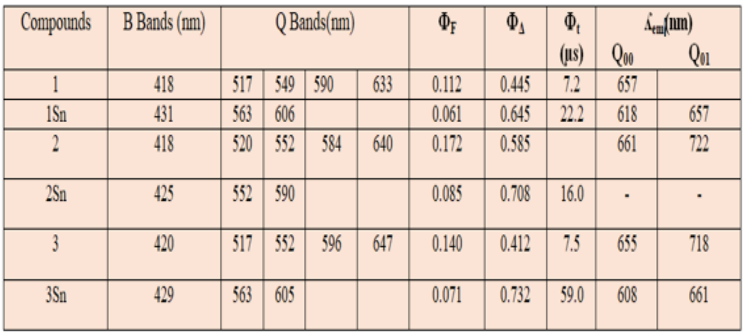
## 3.1. Synthesis

Metal free porphyrins isomers 1, 2 and 3 were synthesized successfully and the yields were about 17%, 20% and 21% respectively. However, tin metallated porphyrins isomers yields were quite straight fowards with 35 %, 40 %, and 36 % for compounds 1 Sn, 2 Sn, and 3 Sn.

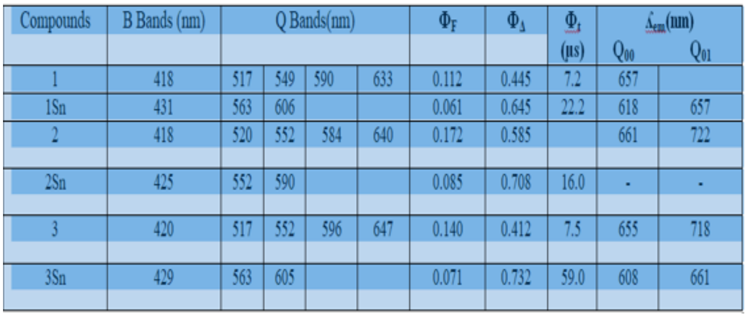
## 3.2. Photophysical properties

Determination of photophysical paremeters was carried out mostly in DMSO and values are reported in table I. It can be seen that all the unmetallated porphyrins show their B-bands almost in the same range (418-420 nm) and four characterisic Q-bands in the range known for simple porphyrins. However, the tin insertion as central metal moved all the B-bands bathochromically (425-431 nm) including the disapearence of two Q-bands in the previous UV spectra related to free bases. (Muthumuni, 2018).

*Table I. Photophysical properties*



| Compounds | B Bands (nm) | Q Bands(nm) | | | | $\Phi_F$ | $\Phi_\Delta$ | $\Phi_t$ (µs) | $\lambda_{em}$(nm) Q$_{00}$ | Q$_{01}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 418 | 517 | 549 | 590 | 633 | 0.112 | 0.445 | 7.2 | 657 | |
| 1Sn | 431 | 563 | 606 | | | 0.061 | 0.645 | 22.2 | 618 | 657 |
| 2 | 418 | 520 | 552 | 584 | 640 | 0.172 | 0.585 | | 661 | 722 |
| 2Sn | 425 | 552 | 590 | | | 0.085 | 0.708 | 16.0 | - | - |
| 3 | 420 | 517 | 552 | 596 | 647 | 0.140 | 0.412 | 7.5 | 655 | 718 |
| 3Sn | 429 | 563 | 605 | | | 0.071 | 0.732 | 59.0 | 608 | 661 |



| Compounds | B Bands (nm) | Q Bands(nm) | | | | $\Phi_F$ | $\Phi_\Delta$ | $\Phi_t$ (µs) | $\lambda_{em}$(nm) Q$_{00}$ | Q$_{01}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 418 | 517 | 549 | 590 | 633 | 0.112 | 0.445 | 7.2 | 657 | |
| 1Sn | 431 | 563 | 606 | | | 0.061 | 0.645 | 22.2 | 618 | 657 |
| 2 | 418 | 520 | 552 | 584 | 640 | 0.172 | 0.585 | | 661 | 722 |
| 2Sn | 425 | 552 | 590 | | | 0.085 | 0.708 | 16.0 | - | - |
| 3 | 420 | 517 | 552 | 596 | 647 | 0.140 | 0.412 | 7.5 | 655 | 718 |
| 3Sn | 429 | 563 | 605 | | | 0.071 | 0.732 | 59.0 | 608 | 661 |

In the other hand the heavy atom effect was demonstrated regarding fluorescence and singlet oxygen quantum yields, where metallation with heavy central metal such as tin into the free unmetallated porphyrins decreases the fluorescence quantum yield by increasing intersystem crossing process and therefore enhance the singlet oxygen quantum yield (Online, 2022 ; Şen, 2013)

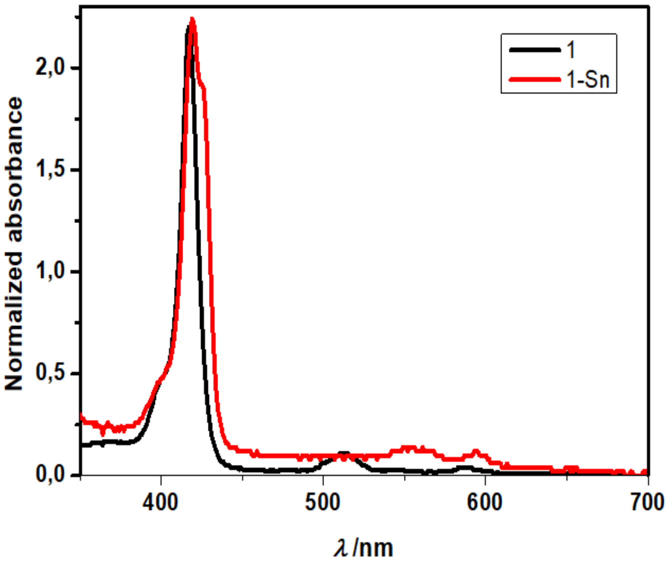


*Figure 2. Normalized UV-Visible absorption spectra of 1 and 1-Sn in DCM.*

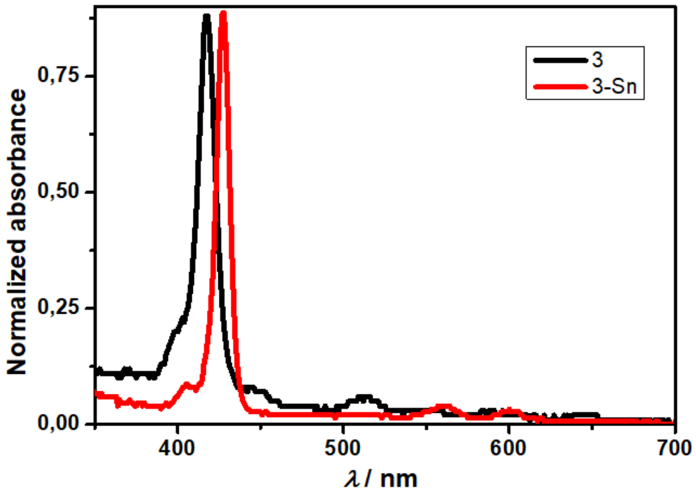


*Figure 3. Normalized UV-Visible absorption spectra of 3 and 3-Sn in DCM.*

### *3.3. Nanosecond laser flash photolysis*

Transient absorption spectra of compounds in DCM, and methanol led to the formation of transients with maximum absorptions in the range of 415–490 nm assigned to the triplet fo compound 3. These results are similar then those reported previously (Barbosa, 2013). figure 4 shows the transient absorption spectra of compounds 3 (~ 5 × $10^{-3}$ M) in aerated dichloromethane recorded 20 ns, 500 ns, and 1 μs after the excitation.

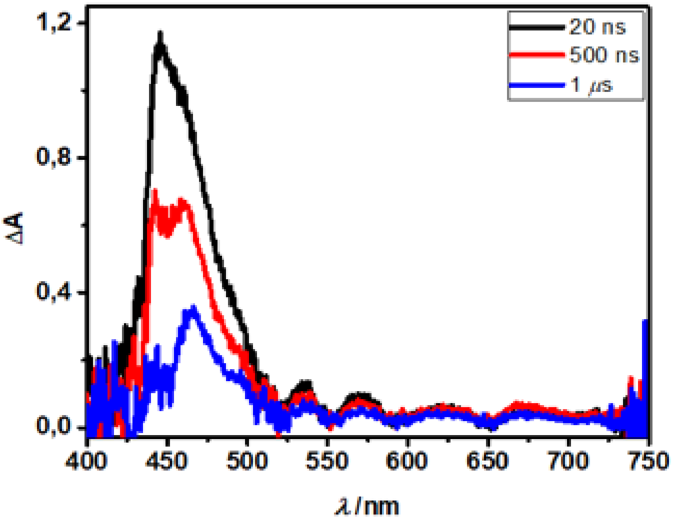
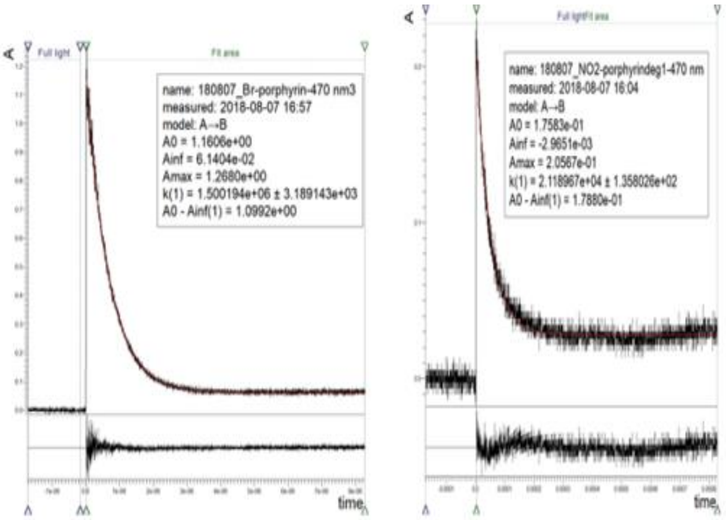


*Figure 4. Transient absorption spectra of compounds of 1 (~ 5 × 10–3 M) in aerated dichloromethane recorded 20 ns, 500 ns, and 1 μs after 355 nm excitation*

Kinetic results have shown that, the rate constants are sensitive in the presence and absence of oxygen by two order of magnitude. The flashfit fitting of compound 2 showed first order kinetic with two different rate constants likely k = 1.50 ×$10^{6}$ $s^{-1}$ and 2.35×$10^{4}$ $s^{-1}$for aerated and degassed DCM respectively (figure 5). This has confirmed the existence of triplet state decay. Similar result (1.58×$10^{6}$M) for other isomers. Triplet lifetimes of porphyrins derivatives have been reported to be in the microsecond scale in aerated solution of chloroform and other solvents (Openda, 2021).



```
name: 180807_Br-porphyrin-470 nm3
measured: 2018-08-07 16:57
model: A→B
A0 = 1.1606e+00
Ainf = 6.1404e-02
Amax = 1.2680e+00
k(1) = 1.500194e+06 ± 3.189143e+03
A0 - Ainf(1) = 1.0992e+00
```

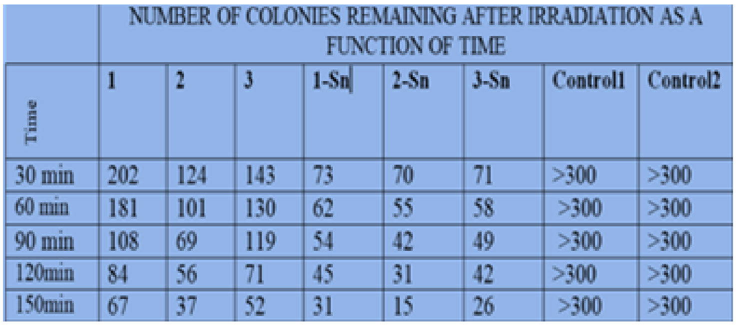
```
name: 180807_NO2-porphyrindeg1-470 nm
measured: 2018-08-07 16:04
model: A→B
A0 = 1.7583e-01
Ainf = -2.9651e-03
Amax = 2.0567e-01
k(1) = 2.118967e+04 ± 1.358026e+02
A0 - Ainf(1) = 1.7880e-01
```

*Figure 5. Triplet decay of **3** in aerated (left) and degassed solution of DCM (right) observed at 470 nm excited at 355 nm.*

### *3.4. In Vitro evaluation of antibacterial activity*

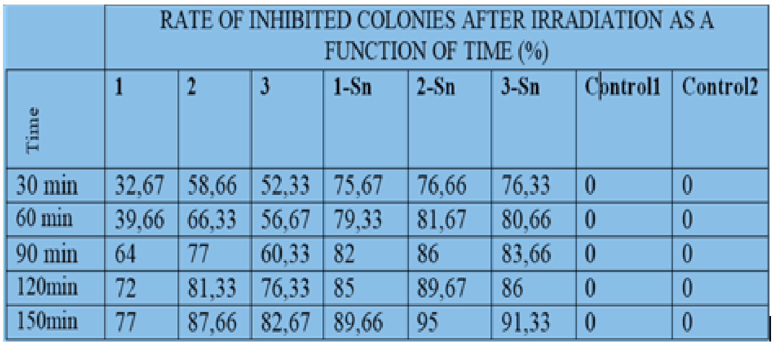
The in vitro antibacterial activity experiments were carried out using compounds **1,2, 3,1-Sn, 2-Sn, 3-Sn** as photosensitzers against *Staphylococcus aureus* (Gram+) and *Escherichia Coli* (Gram –) bacteria in the presence of oxygen. Results are summerized in tables II-III for *Staphylococcus aureus* and tables IV-V for *Escherichia Coli* respectively.

*Table II. Number of Staphylococcus aureus colonies*



| | NUMBER OF COLONIES REMAINING AFTER IRRADIATION AS A FUNCTION OF TIME | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Time | 1 | 2 | 3 | 1-Sn | 2-Sn | 3-Sn | Control1 | Control2 |
| 30 min | 202 | 124 | 143 | 73 | 70 | 71 | >300 | >300 |
| 60 min | 181 | 101 | 130 | 62 | 55 | 58 | >300 | >300 |
| 90 min | 108 | 69 | 119 | 54 | 42 | 49 | >300 | >300 |
| 120min | 84 | 56 | 71 | 45 | 31 | 42 | >300 | >300 |
| 150min | 67 | 37 | 52 | 31 | 15 | 26 | >300 | >300 |

*Table III. Inhibition rate of S. aureus after a specific irradiation time.*



| | RATE OF INHIBITED COLONIES AFTER IRRADIATION AS A FUNCTION OF TIME (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Time | 1 | 2 | 3 | 1-Sn | 2-Sn | 3-Sn | Control1 | Control2 |
| 30 min | 32,67 | 58,66 | 52,33 | 75,67 | 76,66 | 76,33 | 0 | 0 |
| 60 min | 39,66 | 66,33 | 56,67 | 79,33 | 81,67 | 80,66 | 0 | 0 |
| 90 min | 64 | 77 | 60,33 | 82 | 86 | 83,66 | 0 | 0 |
| 120min | 72 | 81,33 | 76,33 | 85 | 89,67 | 86 | 0 | 0 |
| 150min | 77 | 87,66 | 82,67 | 89,66 | 95 | 91,33 | 0 | 0 |

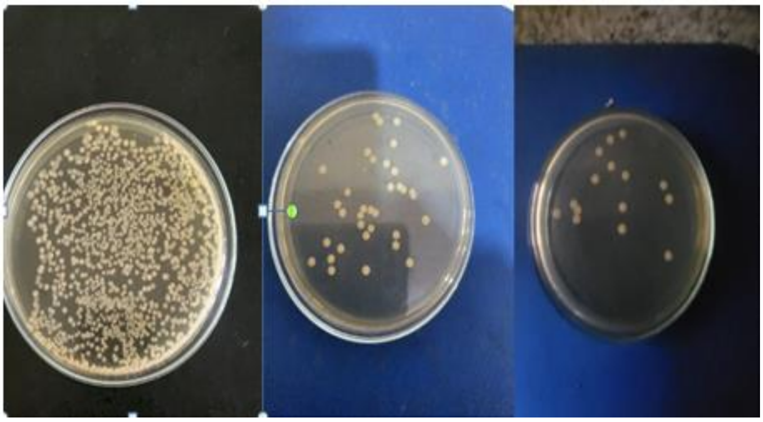
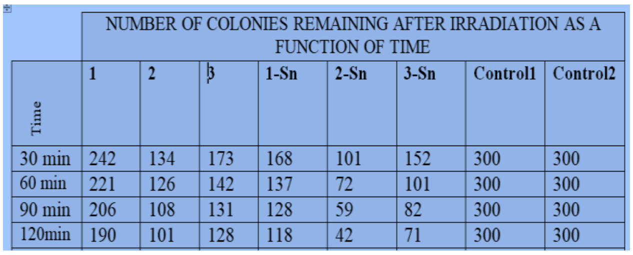


*Figure 6. Images of Staphylococcus aureus at the zero control (LEFT), S. aureus with 1 after 90 min irradiation (MIDDLE) and S. aureus at 150 min irradiation (RIGHT) showing the bacteria colonies*

From tables II and III including figure 8 the disapearence of *Staphylococcus aureus* can be noticed at low concentration such as 2,5 µM. This confirms that the selected porphyrins and their tin metallated porphyrins can be used as photosensitzers to inactivate the development of this gram (+) bacteria (Pomarico, 2018 ; Wardlaw, 2012)

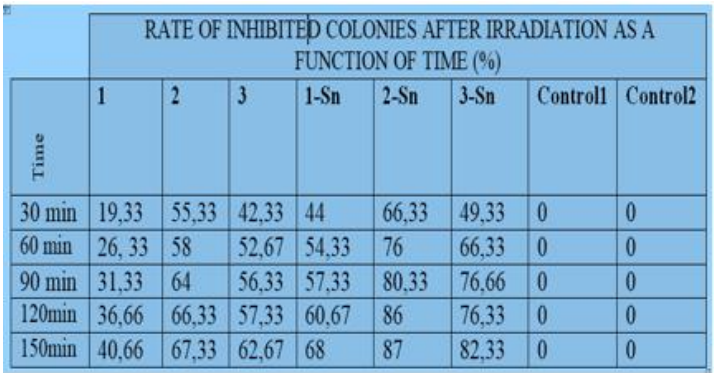
The results obtained for E. coli are shown in the tables (IV - V) below indicating the number of colonies remaining after irradiation with the LED lamp at 632 nm as a function of time and the images in figure 7 illustrate PACT effects of porphyrins on *E. coli*.

*Table IV. Number of E. Coli colonies remaining after irradiation at specific times*



| | NUMBER OF COLONIES REMAINING AFTER IRRADIATION AS A FUNCTION OF TIME | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Time | 1 | 2 | 3 | 1-Sn | 2-Sn | 3-Sn | Control1 | Control2 |
| 30 min | 242 | 134 | 173 | 168 | 101 | 152 | 300 | 300 |
| 60 min | 221 | 126 | 142 | 137 | 72 | 101 | 300 | 300 |
| 90 min | 206 | 108 | 131 | 128 | 59 | 82 | 300 | 300 |
| 120min | 190 | 101 | 128 | 118 | 42 | 71 | 300 | 300 |

*Table V. Inhibition rate of E. Coli after a specific irradiation time*



| | RATE OF INHIBITED COLONIES AFTER IRRADIATION AS A FUNCTION OF TIME (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Time | 1 | 2 | 3 | 1-Sn | 2-Sn | 3-Sn | Control1 | Control2 |
| 30 min | 19,33 | 55,33 | 42,33 | 44 | 66,33 | 49,33 | 0 | 0 |
| 60 min | 26, 33 | 58 | 52,67 | 54,33 | 76 | 66,33 | 0 | 0 |
| 90 min | 31,33 | 64 | 56,33 | 57,33 | 80,33 | 76,66 | 0 | 0 |
| 120min | 36,66 | 66,33 | 57,33 | 60,67 | 86 | 76,33 | 0 | 0 |
| 150min | 40,66 | 67,33 | 62,67 | 68 | 87 | 82,33 | 0 | 0 |

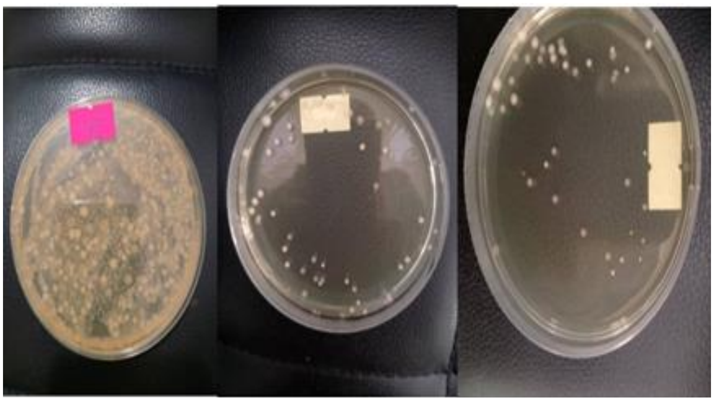


*Figure 7. Images of **Escherichia coli** at the zero control (LEFT), **Escherichia coli** with **1** after 90 min irradiation (MIDDLE) and **Escherichia coli** at 150 min irradiation (RIGHT) showing the bacteria colonies*

Results from table V indicate that all the used selected porphyrins can inactivate E Coli development after 632 nm light dose 77 J/cm$^2$ irradiation using LED. These results confirm the heavy atom effect comparing free unmetallated and tin metallated porphyrins. Similar PDT results were obtained with these kind of porphyrins using different central metals such as Zn an Ga (Muthumuni, 2019).

## 4. Conclusion

Free meso-tetrakis (2-bromophenyl), meso-tetrakis (3-bromophenyl) and meso-tetrakis (4-bromophenyl) porphyrins along with their tin inserted porphyrins have been studies as potential candidate as photosensitisers for multiresistent bacteria eradication. These six compounds have shown some promising results from singlet oxygen quantum yield which is related to antimicrobial activity especially against gram negative (*E. Coli*) and gram positive (*Staphylococcus aureus*). Nanosecond laser flash photolysis have shown that porphyrins derivatives after excitation at 355 nm they are absorbing light from ground state to singlet state and then there is an intersystem crossing which allows the triplet state formation in the range of microsecond scale either for methanol, phosphate buffer or dimethylsulfoxide solutions used as solvents.

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## Conflicts of interest

There are no conflicts to mention.

## Ethical consideration

We are committed to respecting essential ethical principles in the writing of this article.

## Authors contributions

M.M and G.K synthesized compound 1,2 and 3 respectively at different time.

G.S made all the photophysical experiments.

B.N has designed the synthesis of free base porphyrin including participation to the writing of the maniscript.

J.M and T.N did a great contribution to provide chemical and preparing maniscript.

K.N and K.T substantially contributed by supervising and coonceptualizing the work.

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## SUPPORTING INFORMATION

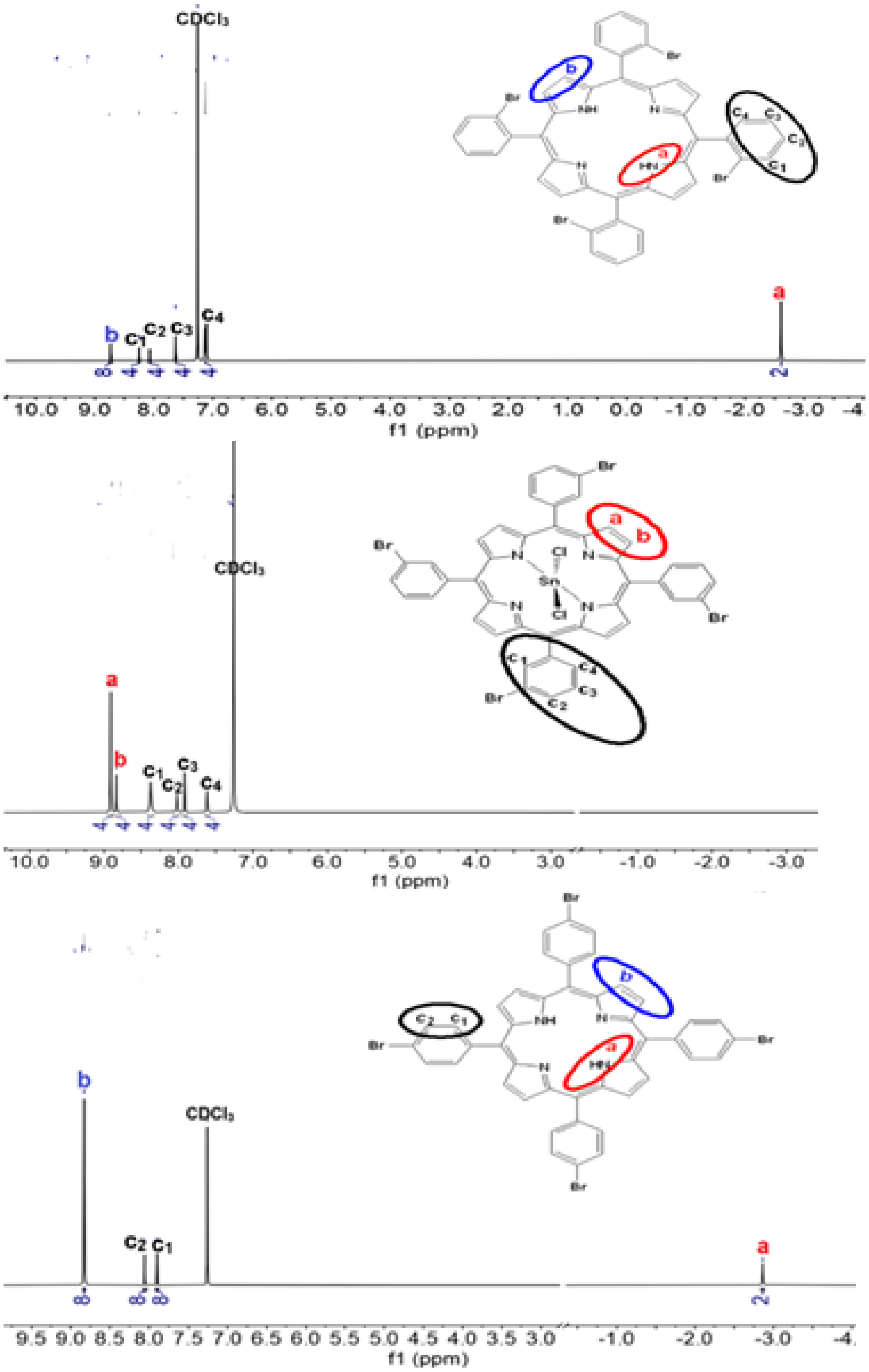
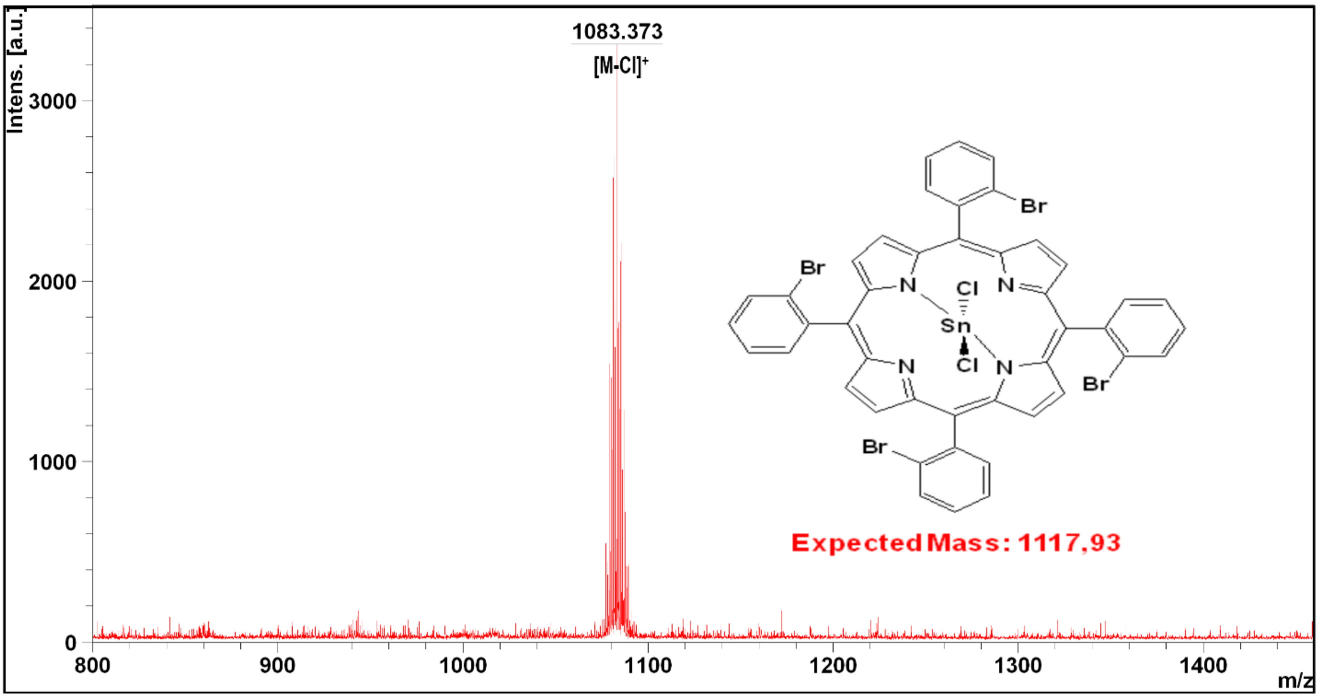


*Figure S1. 1HNMR of the synthesized compounds*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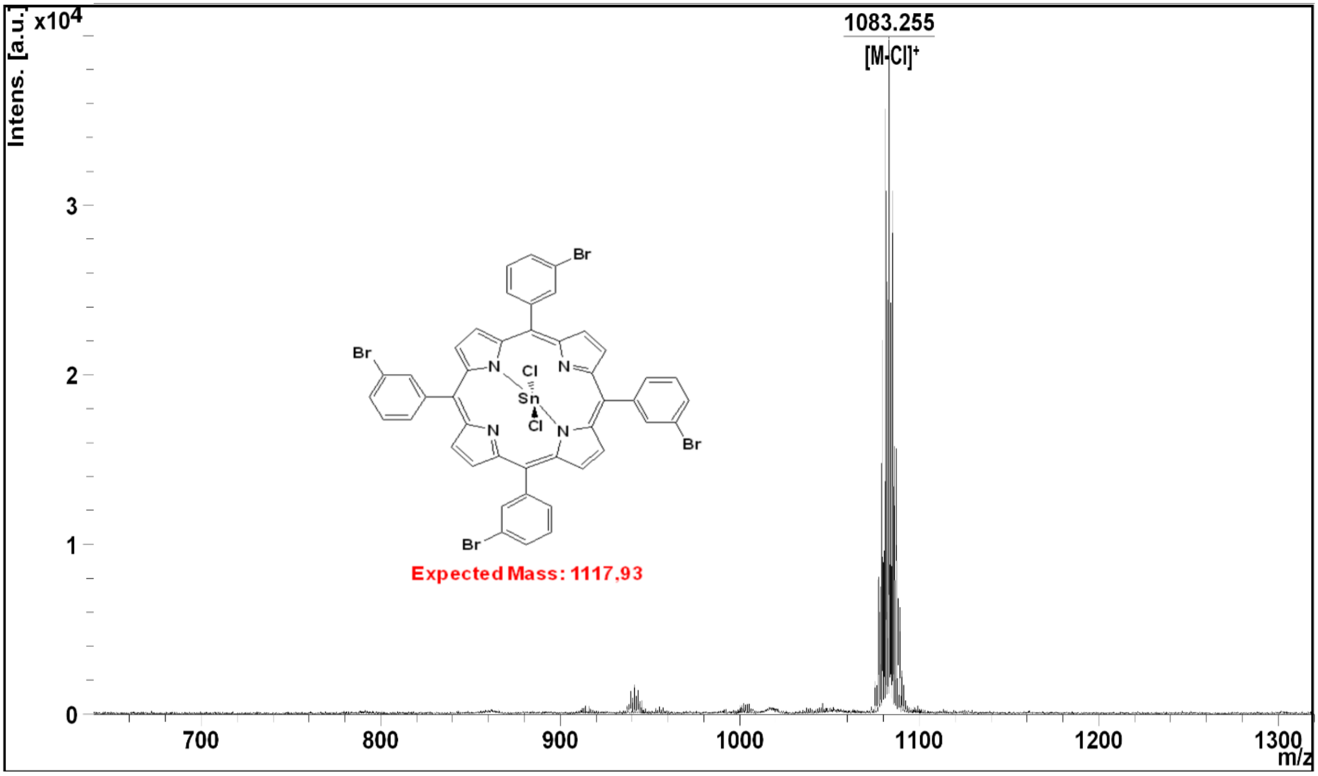
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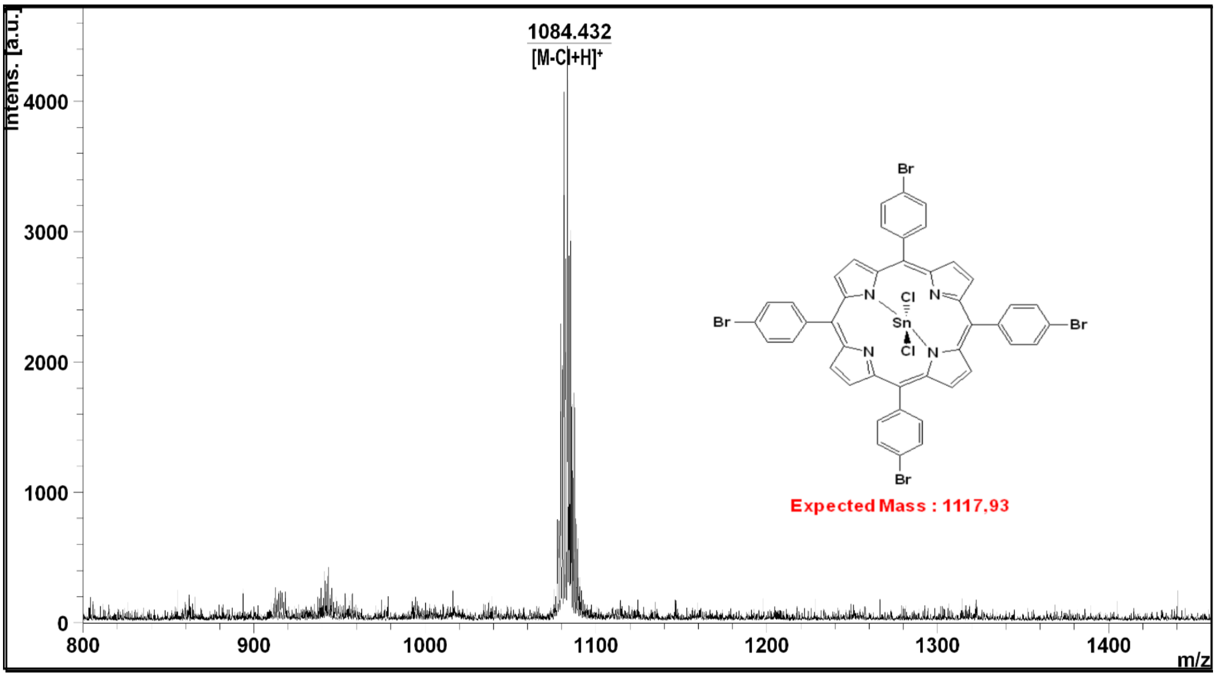


*Figure S2*. *MALDI-TOF of the synthesized compounds*

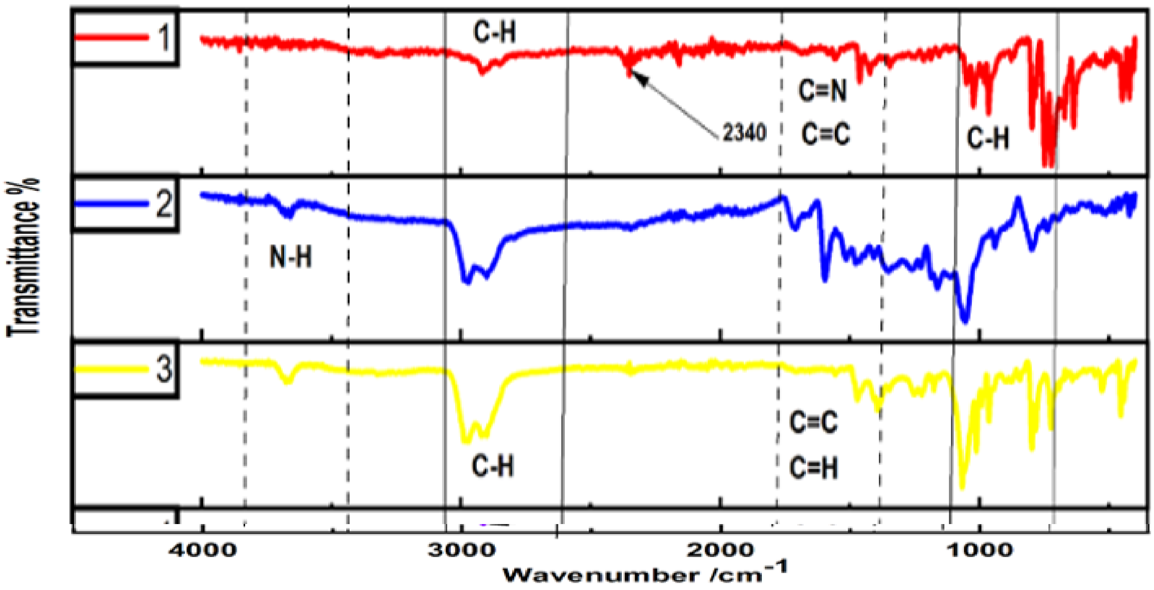


*Figure S3*. *FT-IR of the synthesized compounds*

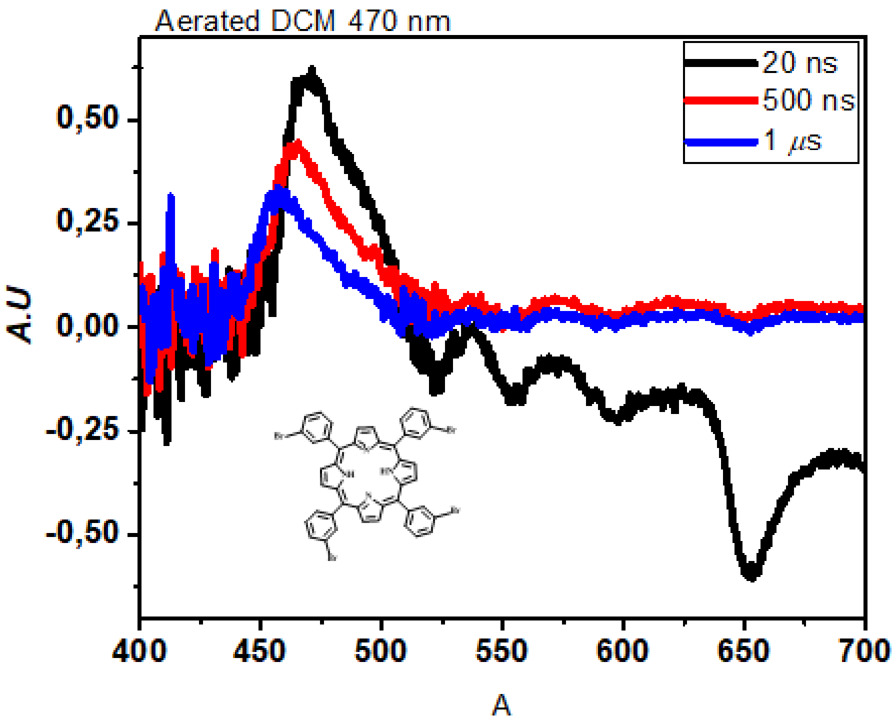
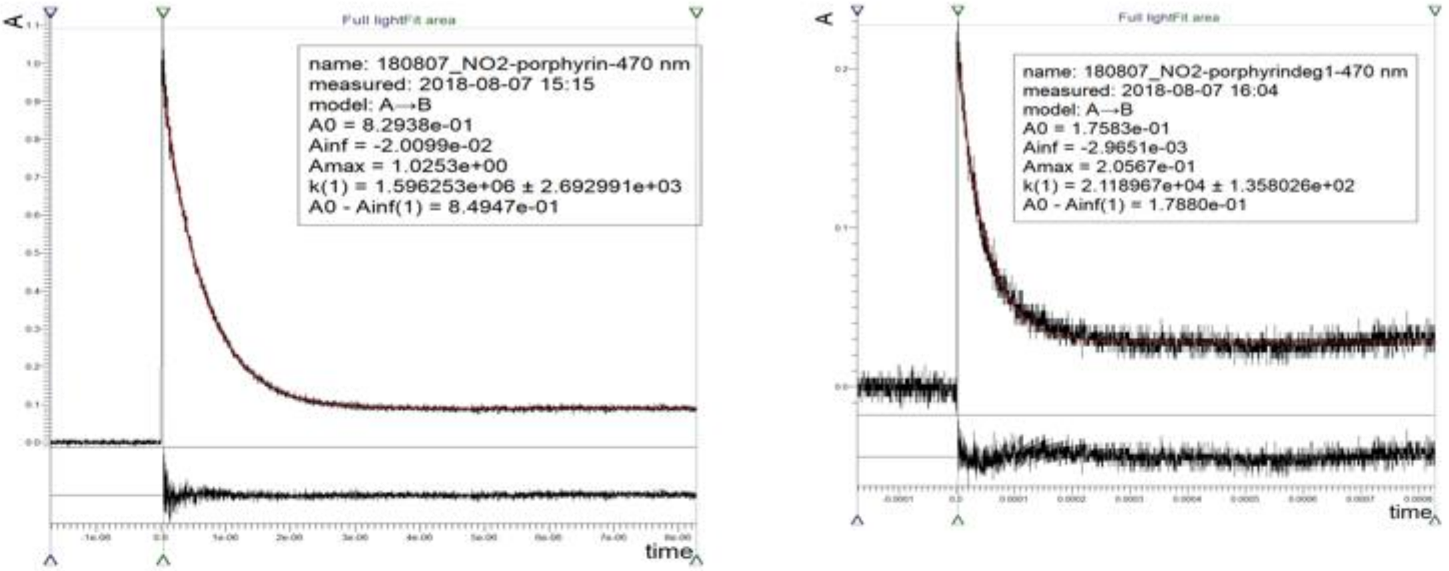


*Figure S4***.** *Transient absorption spectra of compounds of* ***3*** *(~ 6 × $10^{-3}$ M) in aerated dichloromethane recorded 20 ns, 500 ns, and 1 μs after 355 nm excitation*



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measured: 2018-08-07 15:15
model: A→B
A0 = 8.2938e-01
Ainf = -2.0099e-02
Amax = 1.0253e+00
k(1) = 1.596253e+06 ± 2.692991e+03
A0 - Ainf(1) = 8.4947e-01

name: 180807_NO2-porphyrindeg1-470 nm
measured: 2018-08-07 16:04
model: A→B
A0 = 1.7583e-01
Ainf = -2.9651e-03
Amax = 2.0567e-01
k(1) = 2.118967e+04 ± 1.358026e+02
A0 - Ainf(1) = 1.7880e-01

*Figure S5. Triplet decay of* ***2*** *in aerated (left) and degassed solution of DCM (right) observed at 470 nm excited at 355 nm.*

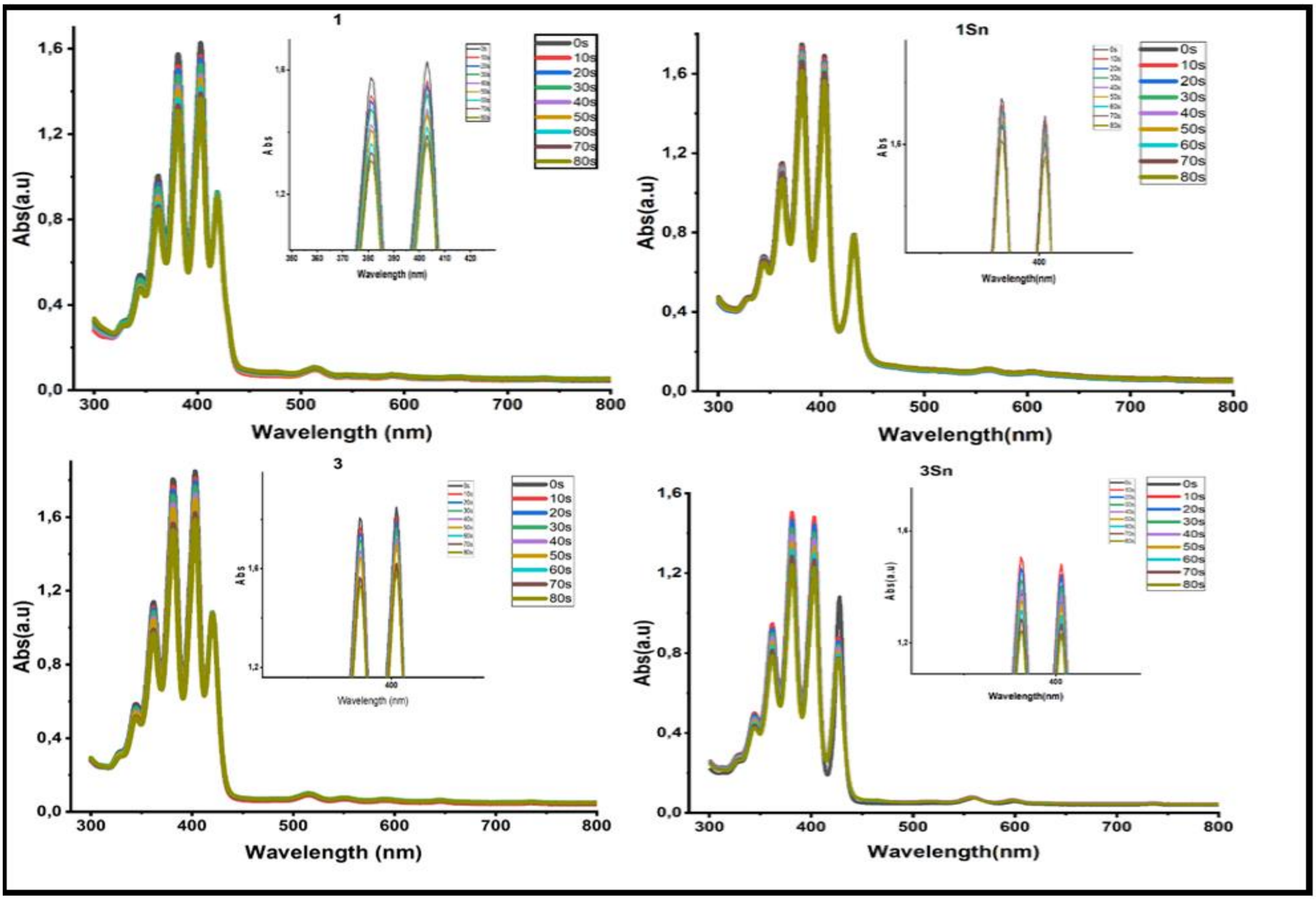

*Figure S6*. *Shows Singlets oxygen graph of 1, 1Sn, 3, and 3Sn*