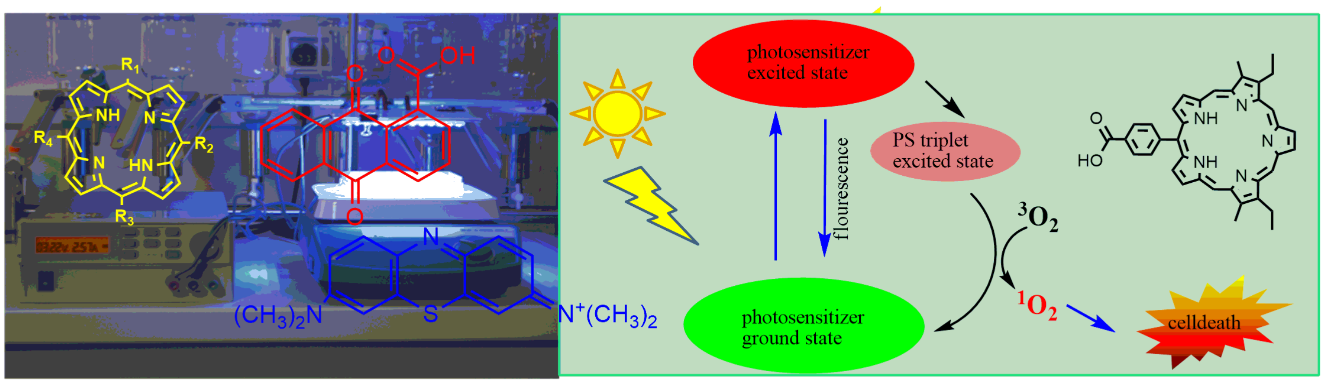
UNIVERSITÀ DEGLI STUDI DI UDINE

DOTTORATO DI RICERCA IN

TECNOLOGIE CHIMICHE ED ENERGETICHE

CICLO XXVII

SYNTHESIS AND CHARACTERIZATION OF NEW ORGANIC MATERIALS WITH POTENTIAL APPLICATION IN WATER TREATMENT



PhD defense: 12/04/16

PhD student- Merlyn Mathilda Thandu

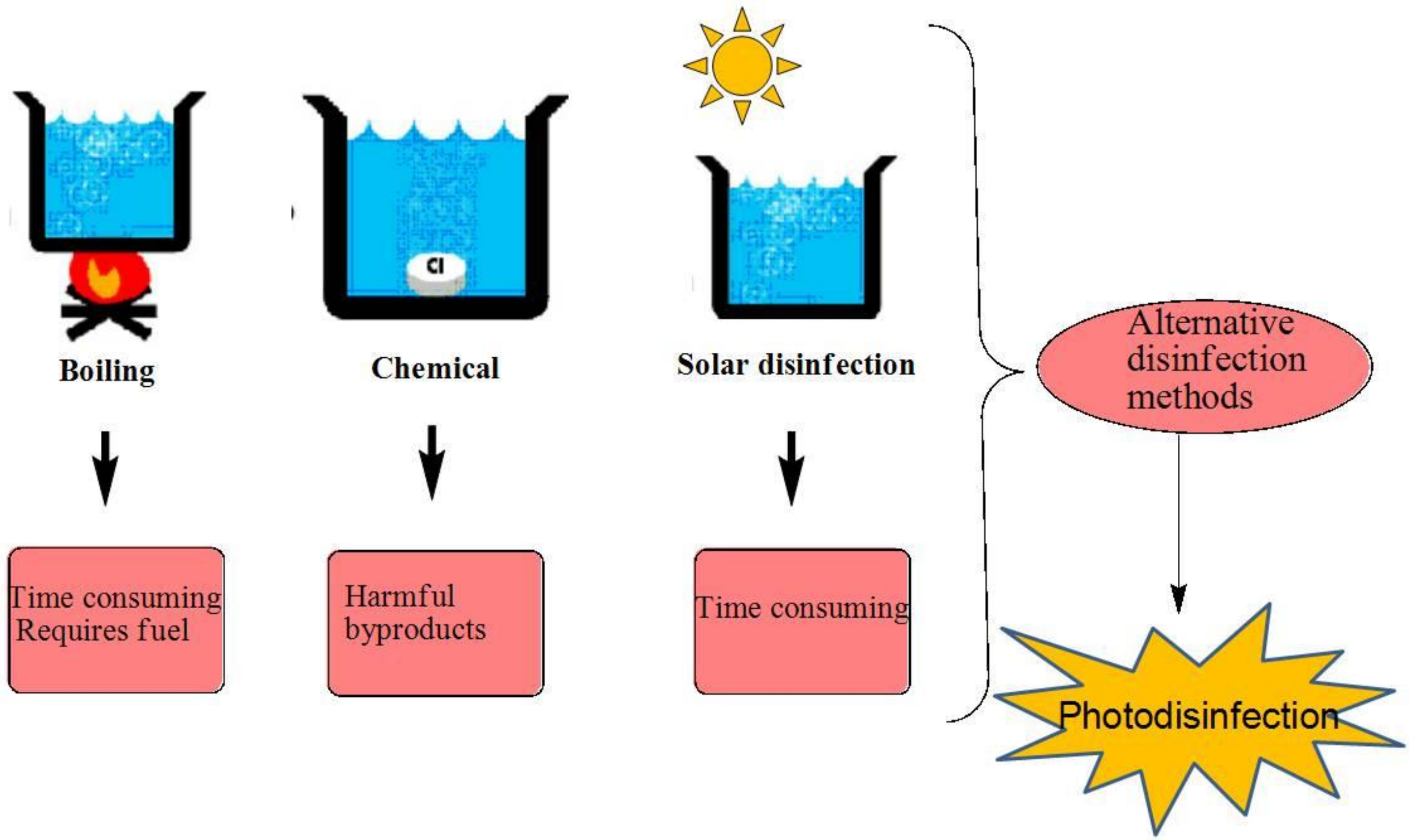
Supervisor- Prof. Daniele Goi

Co-supervisor- Dr. Clara Comuzzi

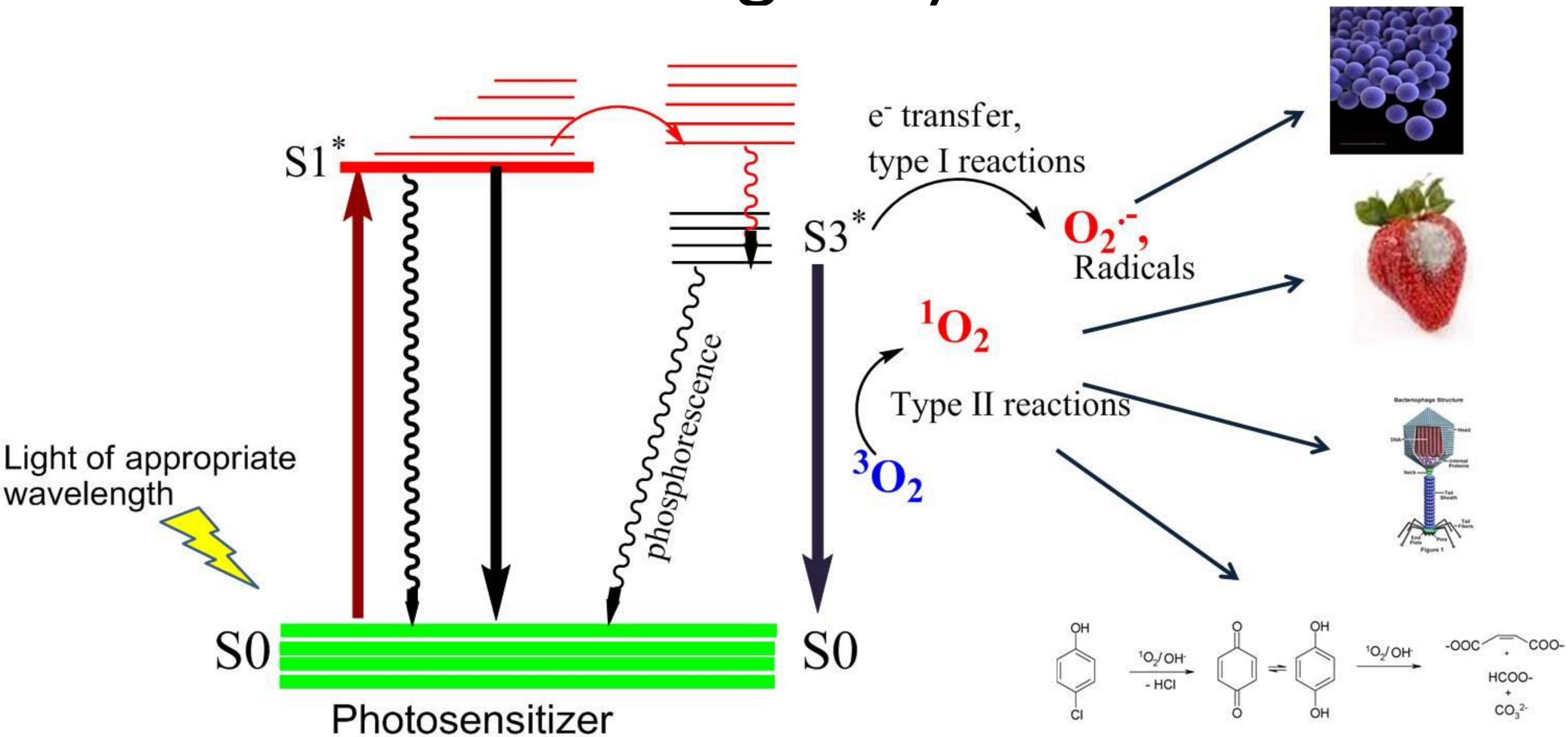
Outline of the project

- Trial syntheses of new organic photosensitizers
- Incorporation of photosensitizers onto solid supports and evaluation of their photo efficiency
  - Immobilization of TPP on magnetic nanoparticles
  - Polyvinylchloride (PVC) supported TPP
  - Polyvinylchloride (PVC) supported PCCox

Conventional methods of water purification

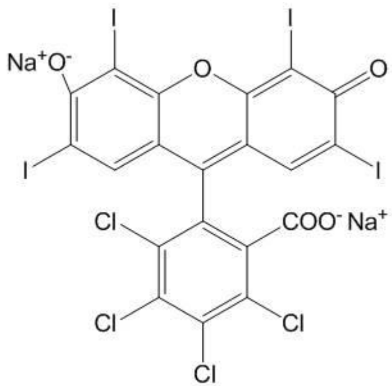


Photosensitization process (Jablanski diagram)

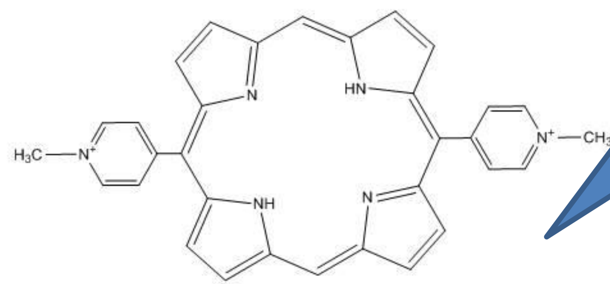


Thandu, M., Comuzzi, C., Goi, D., et al. “Phototreatment of water by organic photosensitizers and comparison with inorganic semiconductors” *International Journal of Photo Energy*, Volume 2015 Article ID 521367, pages 22

Common photosensitizers

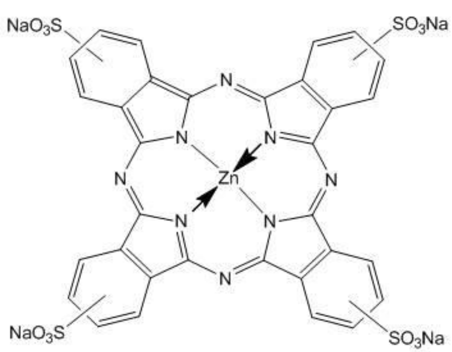


Rose Bengal (RB)

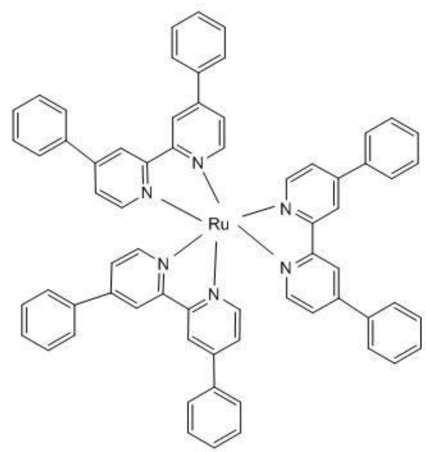


5,15-Di(N-methyl-4-pyridinium) porphyrin (DMPyP)

well known for their use in (Photodynamic therapy) PDT and antimicrobial therapy

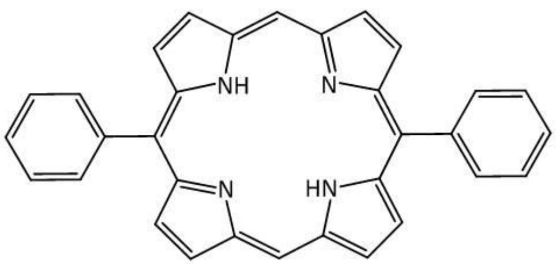


Zinc(II) phthalocyanine tetrasulfonic acid tetrasodium salt (ZnPcS)



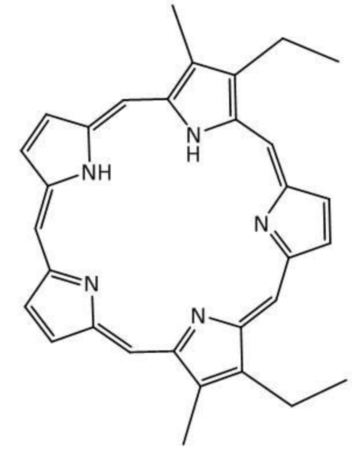
Tris (4,4'-diphenyl-2,2'- bipyridine)ruthenium(II)(RDB^{2+})

Expanded porphyrins- new class of photosensitizers

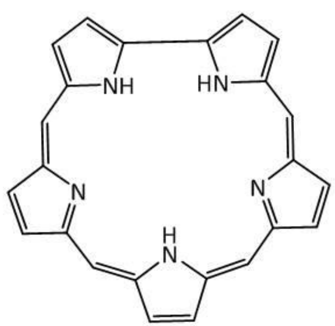


Porphyrin 18 π electrons

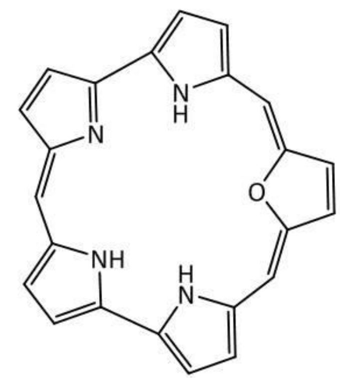
- Increased degree of conjugation
- Absorption spectrum- red shift
- Wide range of applications
- Co-ordination with large metal ions



Pentaphyrin 22 π electrons



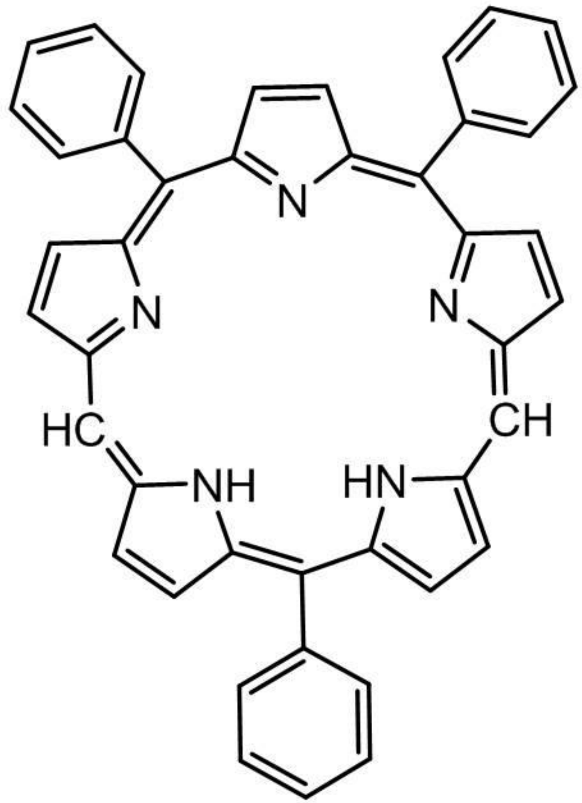
Sapphyrin 22 π electrons



Smaradyrin 22 π electrons

Molecular structure of fully oxidized pentaphyrin

The target pentaphyrin

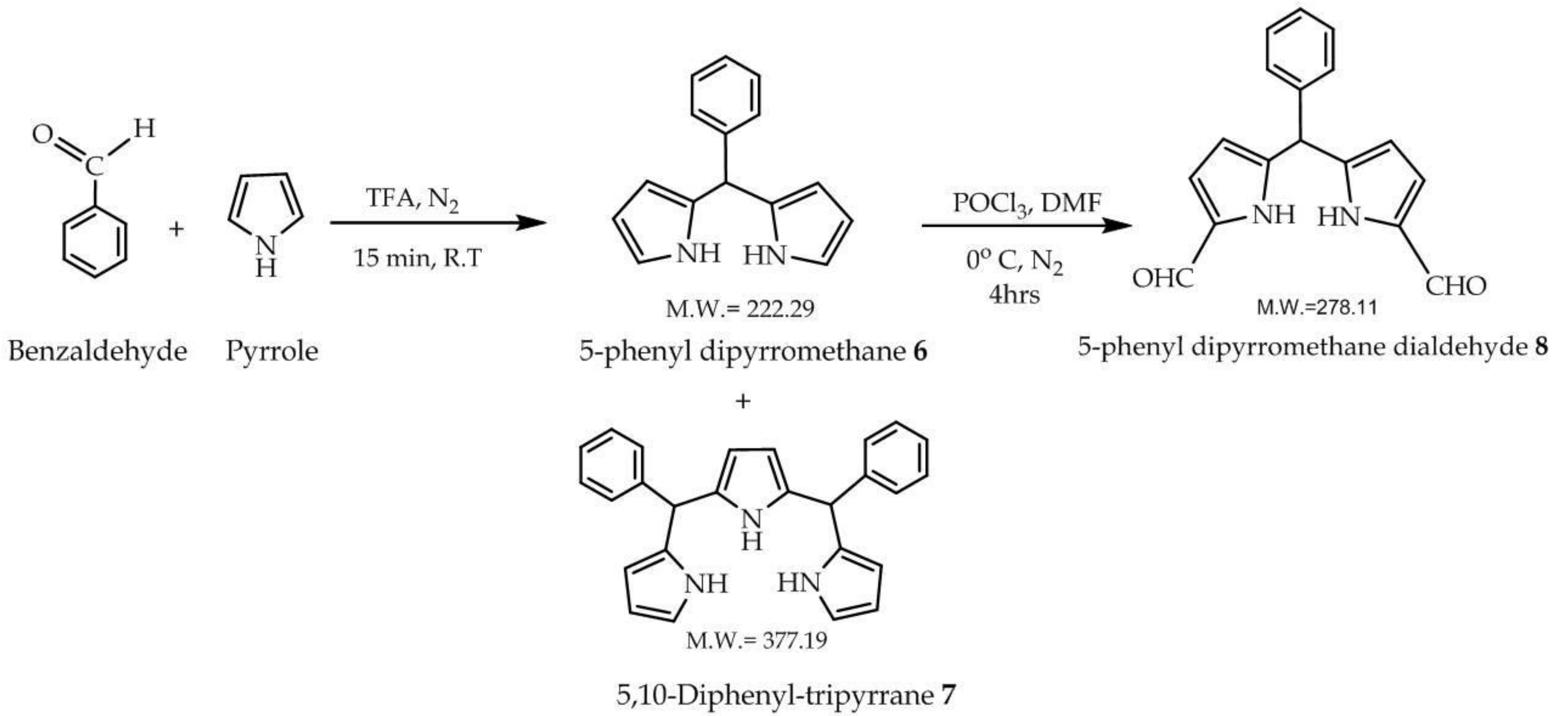


M.W.= 615.24

22 π electron system

Synthesis of precursors

Synthesis of 5-phenyl dipyrromethane and 5,10-diphenyl-tripyrrane

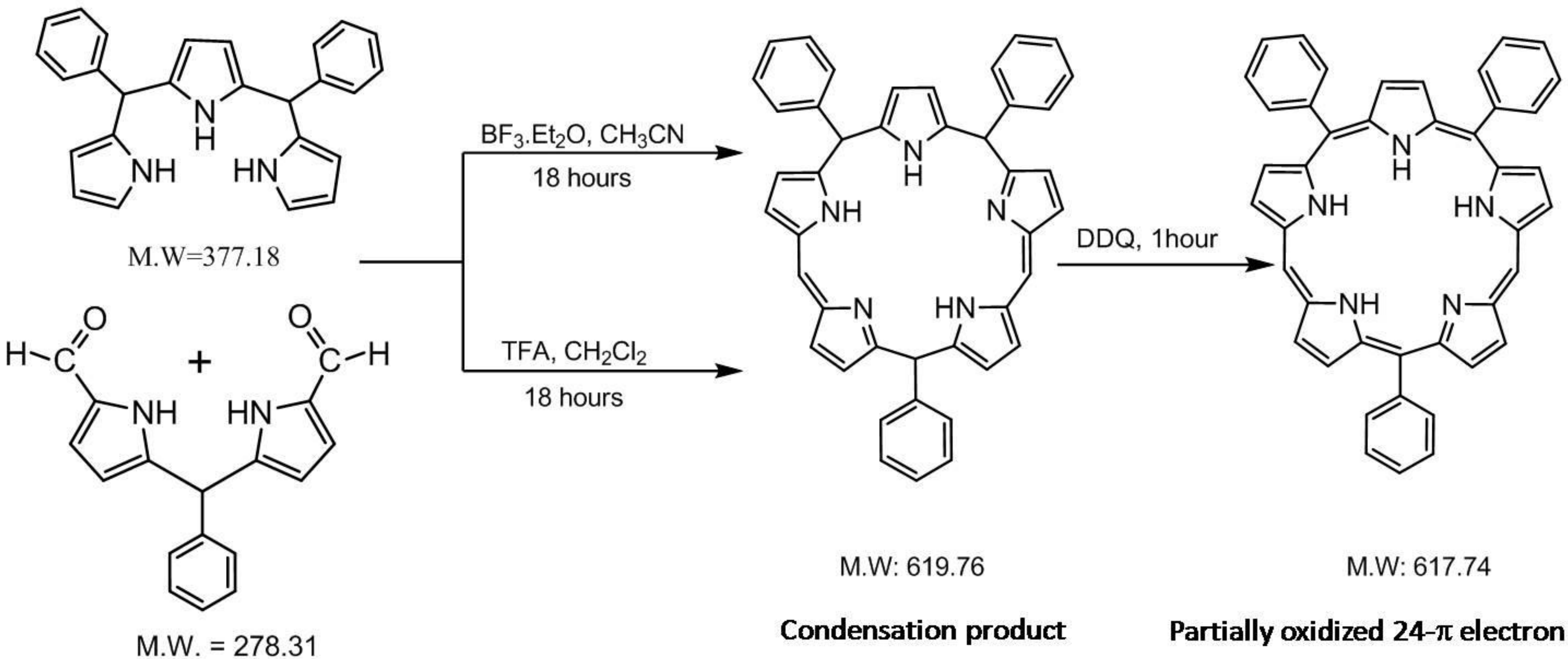


Compound **6** ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): δ= 5.4 (s, 1H), 5.88 (m, 2H), 6.13(q, 2H), 6.61 (q, 2 H), 7.26 (m, 5 H), 7.82(br s, 2H).

Compound **7** ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): δ=5.40 (s, 2H), 5.93 (q, 2H), 6.05 (m, 2H), 6.30 (q, 2H), 6.71 (dd, 2H), 7.44 (m, 10H), 7.97 (br s, 3H)

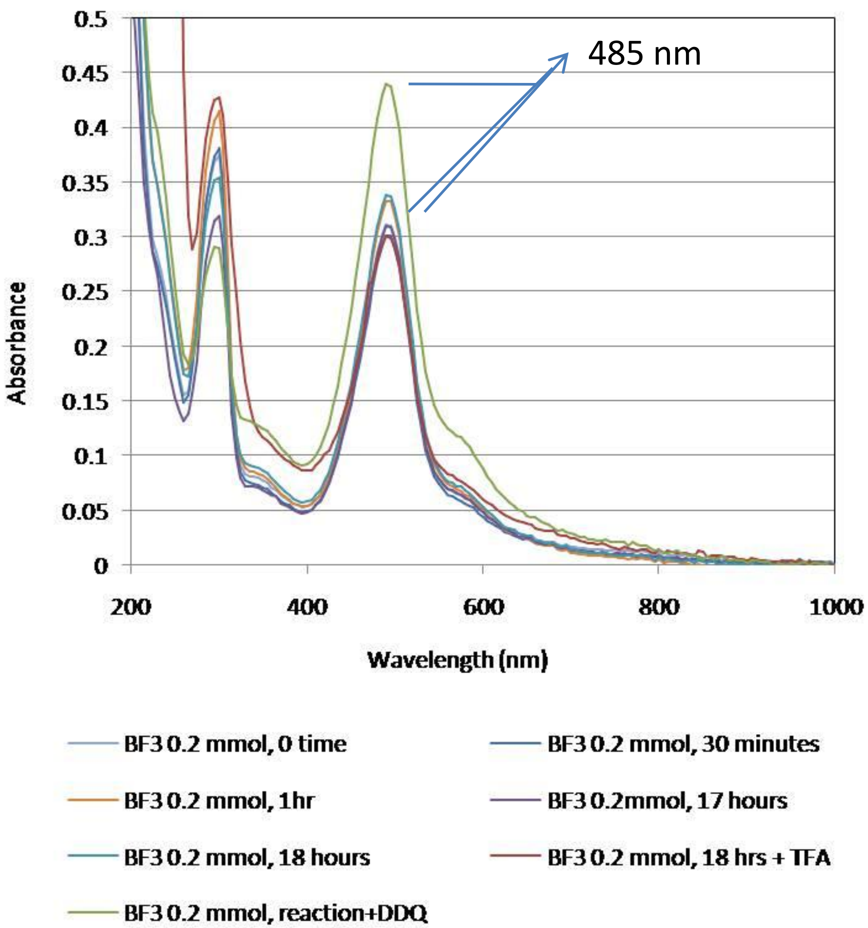
Compound **8** ^{1}H NMR ((200 MHz, $CDCl_3$, 25°C): δ=5.59 (s, 1H), 6.03 (q, 2H), 6.83 (q, 2H), 7.27 (m, 5H), 9.14 (s, 5 H), 10.88 (br s, 2 H)).

Synthesis of triphenyl pentaphyrin

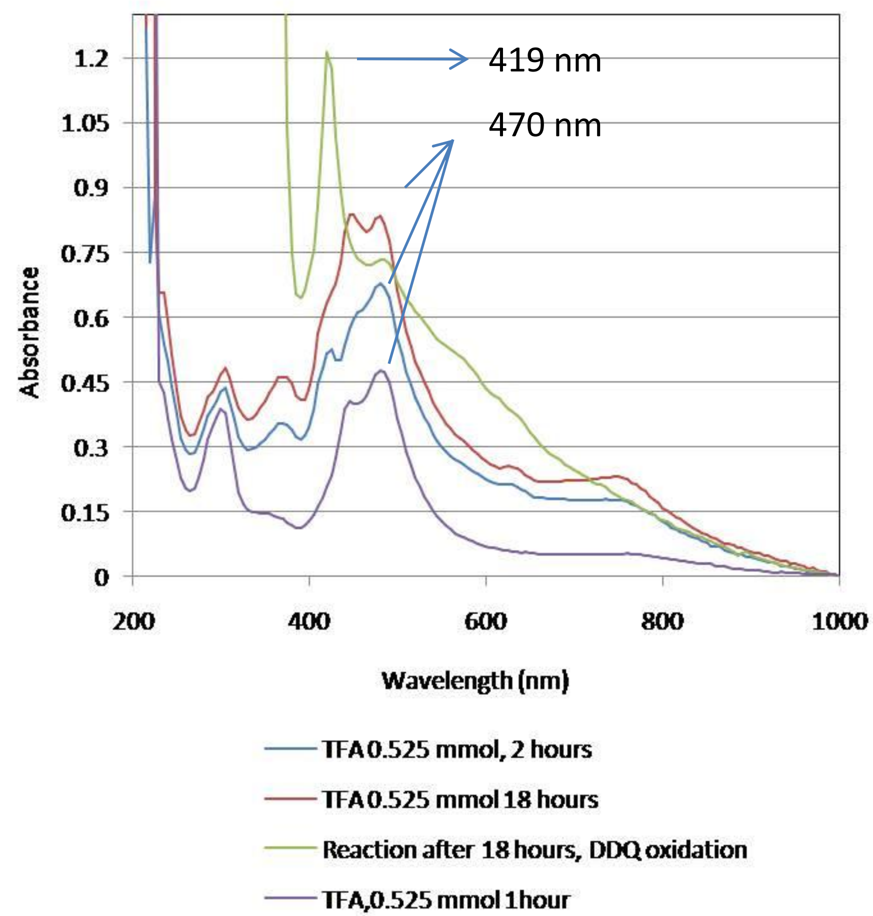


UV-visible spectral changes

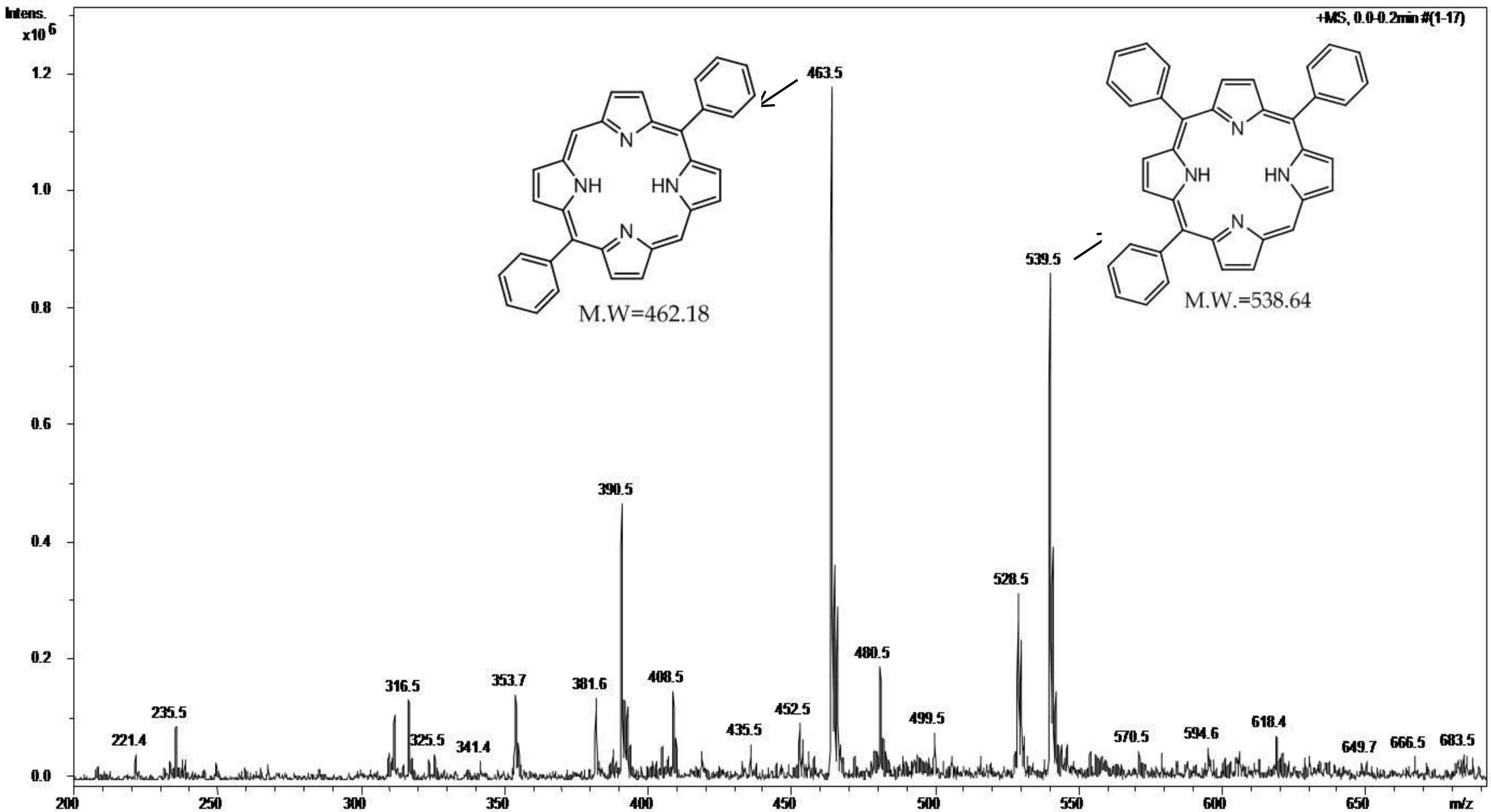
BF3 catalysed



TFA catalysed

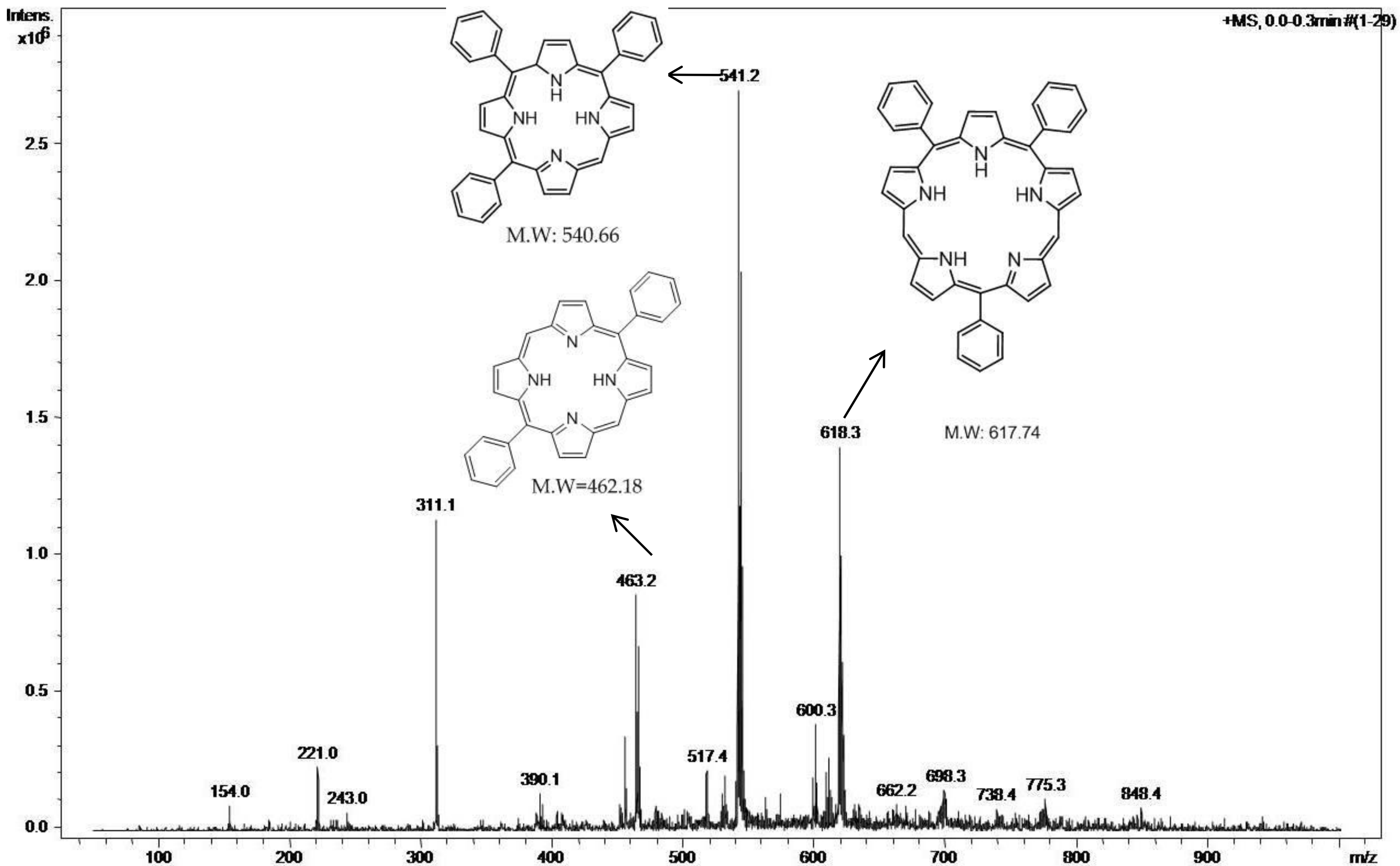


Mass spectrum of BF_3 catalysed reaction

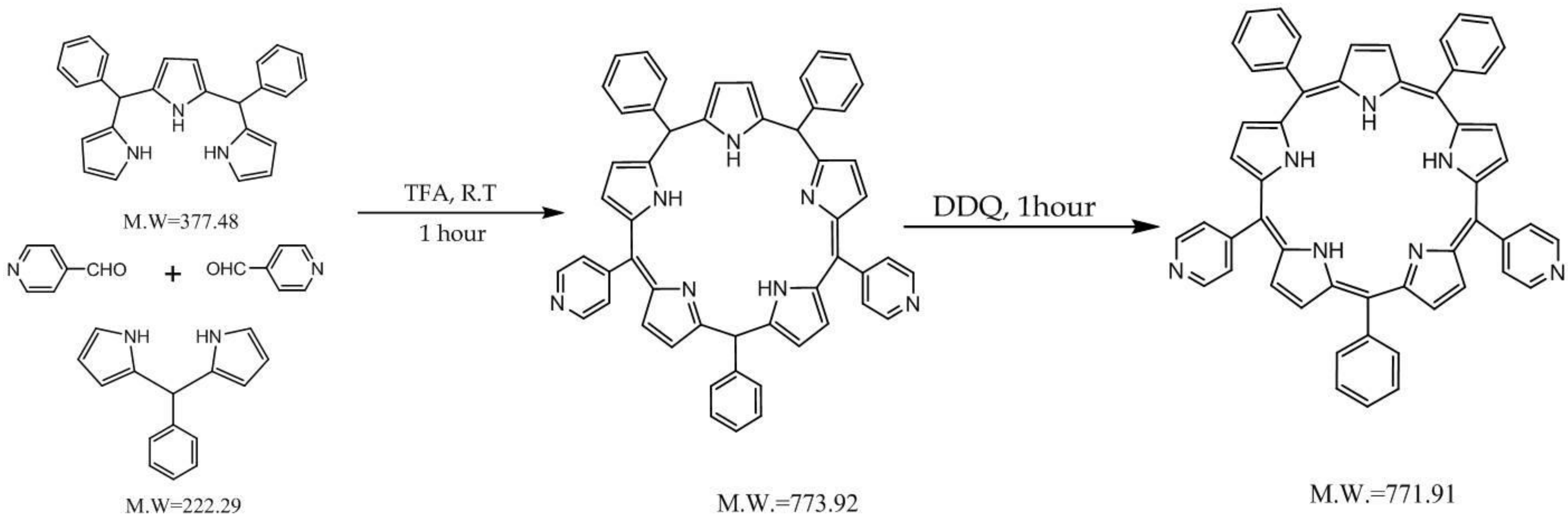


[1]H NMR ($CDCl_3$), δ= –3.01 (br s, 2H), 7.80 (m, 9 H), 8.28 (dd, 6 H), 9.08 (d, 4H), 9.37 (d, 4H), 10.30 (s, 1H).

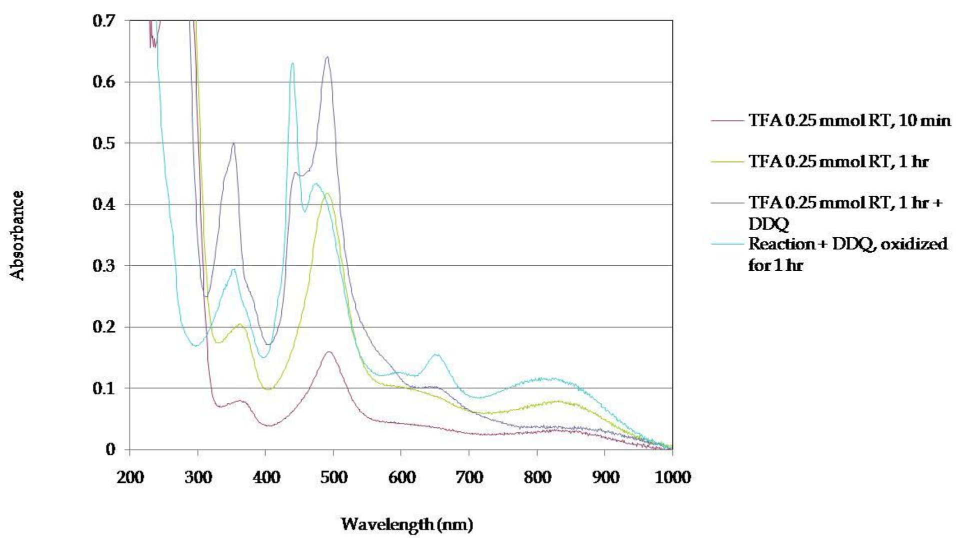
Mass spectrum of TFA catalysed reaction



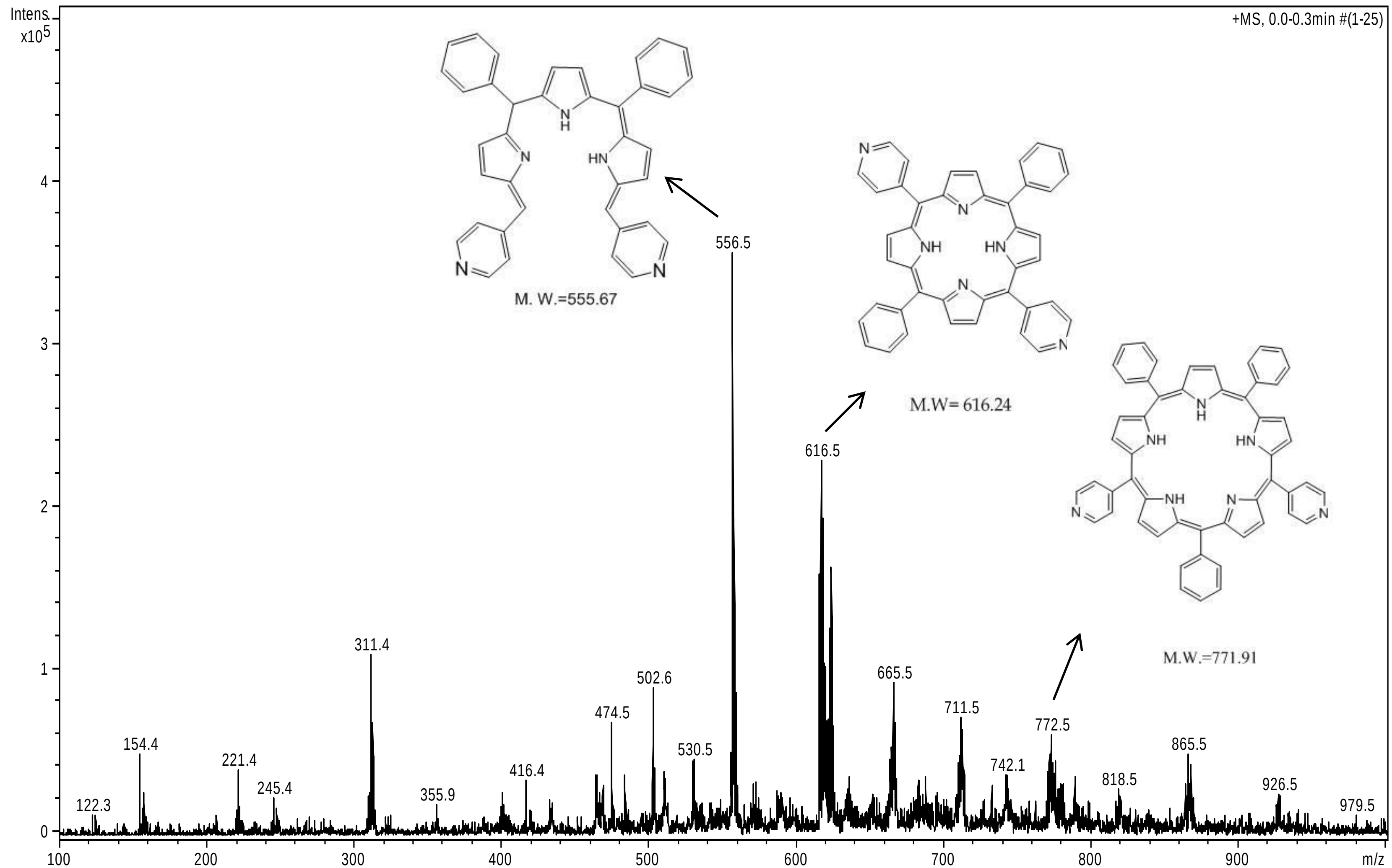
Synthesis of pyridine substituted pentaphyrin



24 π electron system

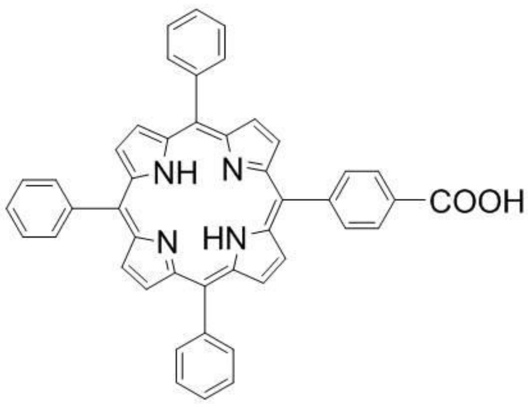


ESI-mass spectrum of the oxidized product

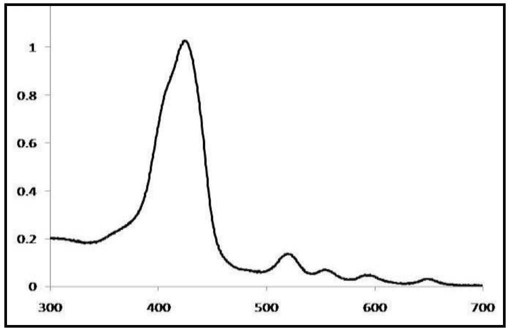


Photosensitizers used for immobilization

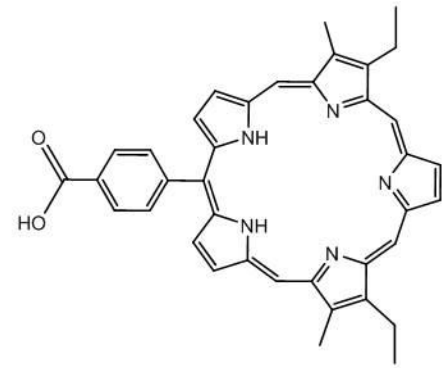
A well-known commercially available porphyrin



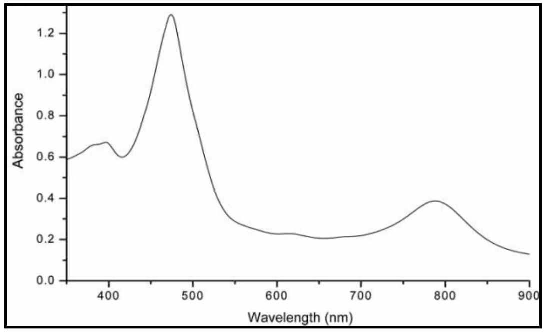
5-(4-Carboxyphenyl)-10,15,20-triphenyl-21,23H-porphyrin (TPP)



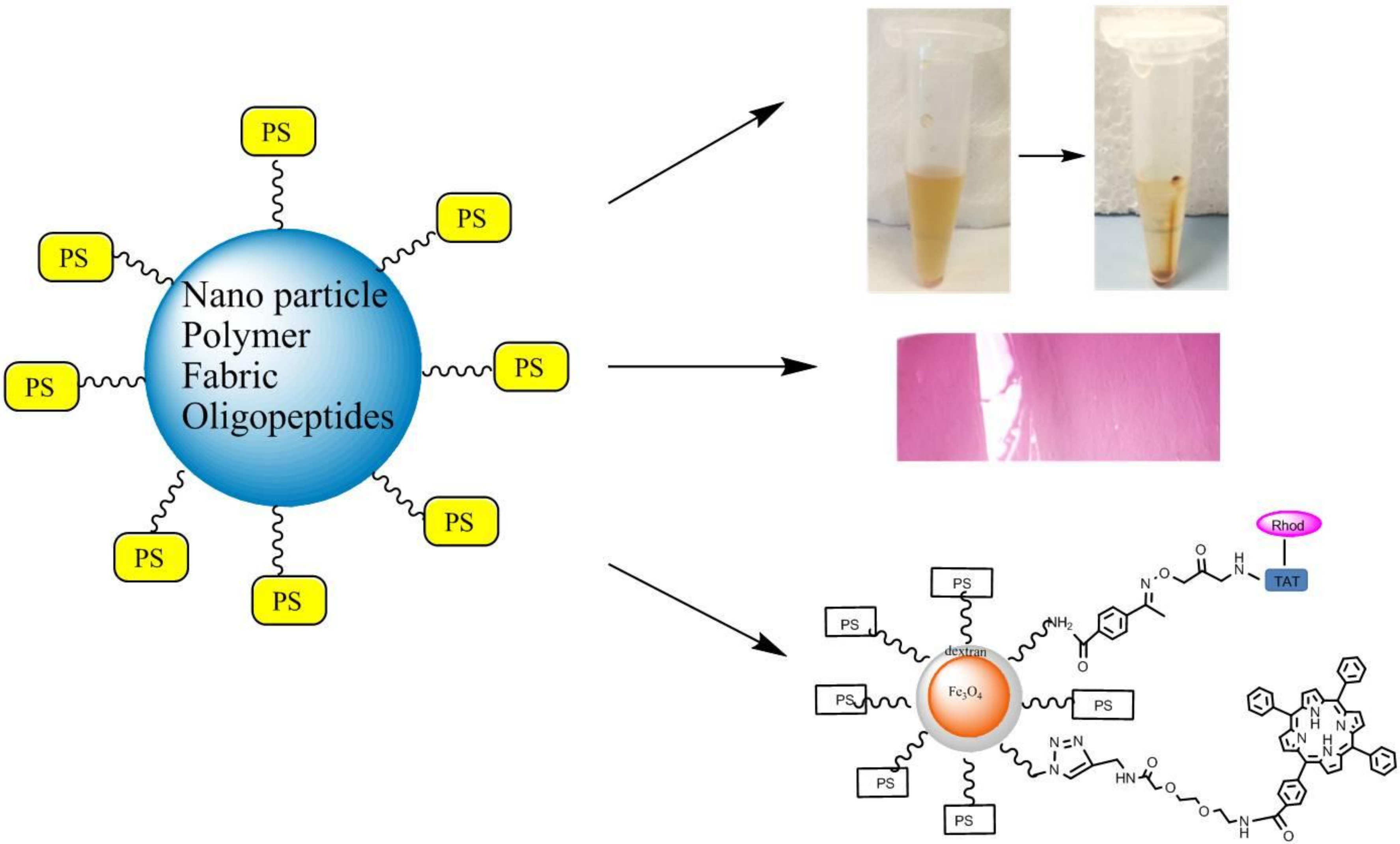
Pentaphyrin previously synthesized in lab and successfully tested for photodisinfection



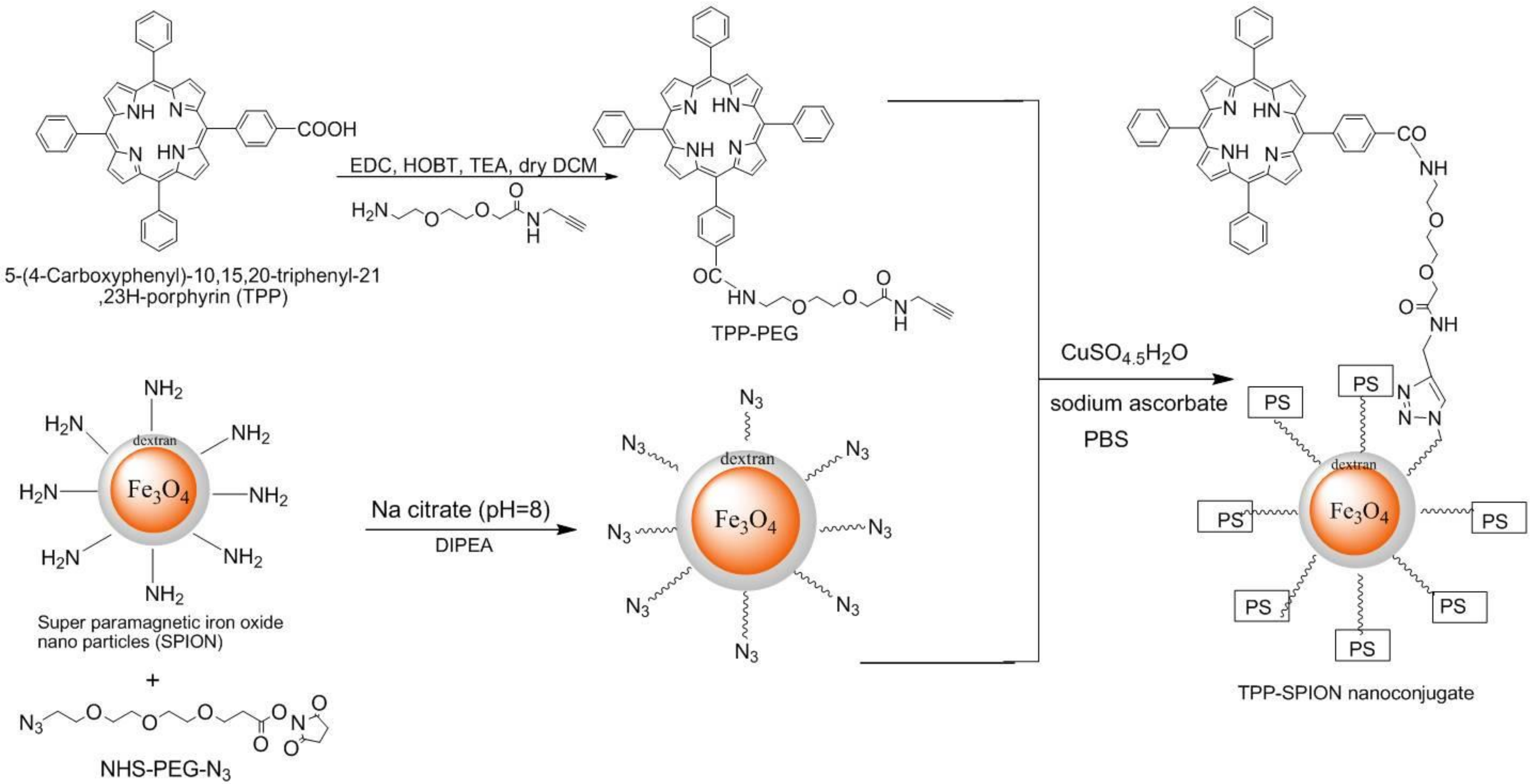
20-(4-carboxyphenyl)-2,13-dimethyl-3, 12-diethyl-(22p) pentaphyrin (PCCox)



Applications of PS immobilization

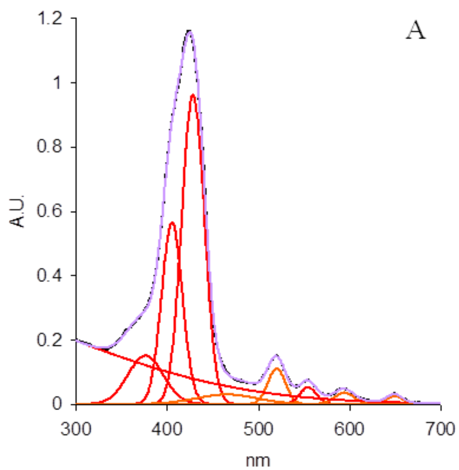


Synthesis of magnetic TPP-SPION nanoconjugate/click reaction

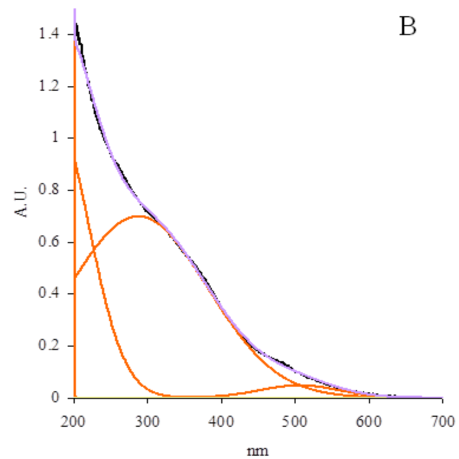


Thandu, M., Rapozzi, V., Xodo, L., Albericio, F., Comuzzi, C. and Cavalli, S. , “Clicking” Porphyrins to Magnetic Nanoparticles for Photodynamic Therapy. *ChemPlusChem*., volume 70, 90-98, 2014, doi: 10.1002/cplu.201300276

Characterization of SPION-TPP:UV-visible analysis



6µM TPP in PBS



SPION in PBS

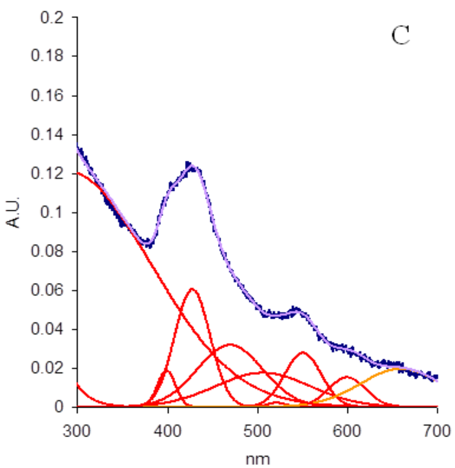
$A = \varepsilon . c . l$

$\varepsilon = 1.43 \times 10^5\ M^{-1}\ cm^{-1}$

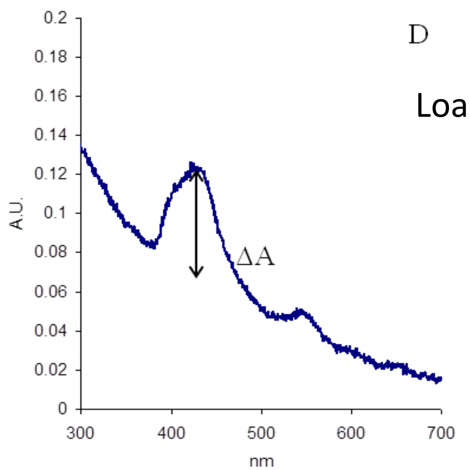
$\Delta A = A_{TPP-SPION} - A_{SPION}$

Concentration of SPION-TPP by the deconvolution method = 3.87 µM

Number of nano particles per ml (in stock solution of TPP-SPION) = 8×10^3



50 µl SPION-TPP in 450 µl PBS (blue line)
With deconvolution of individual bands(red lines)
and the calculated convolution spectrum (purple line)

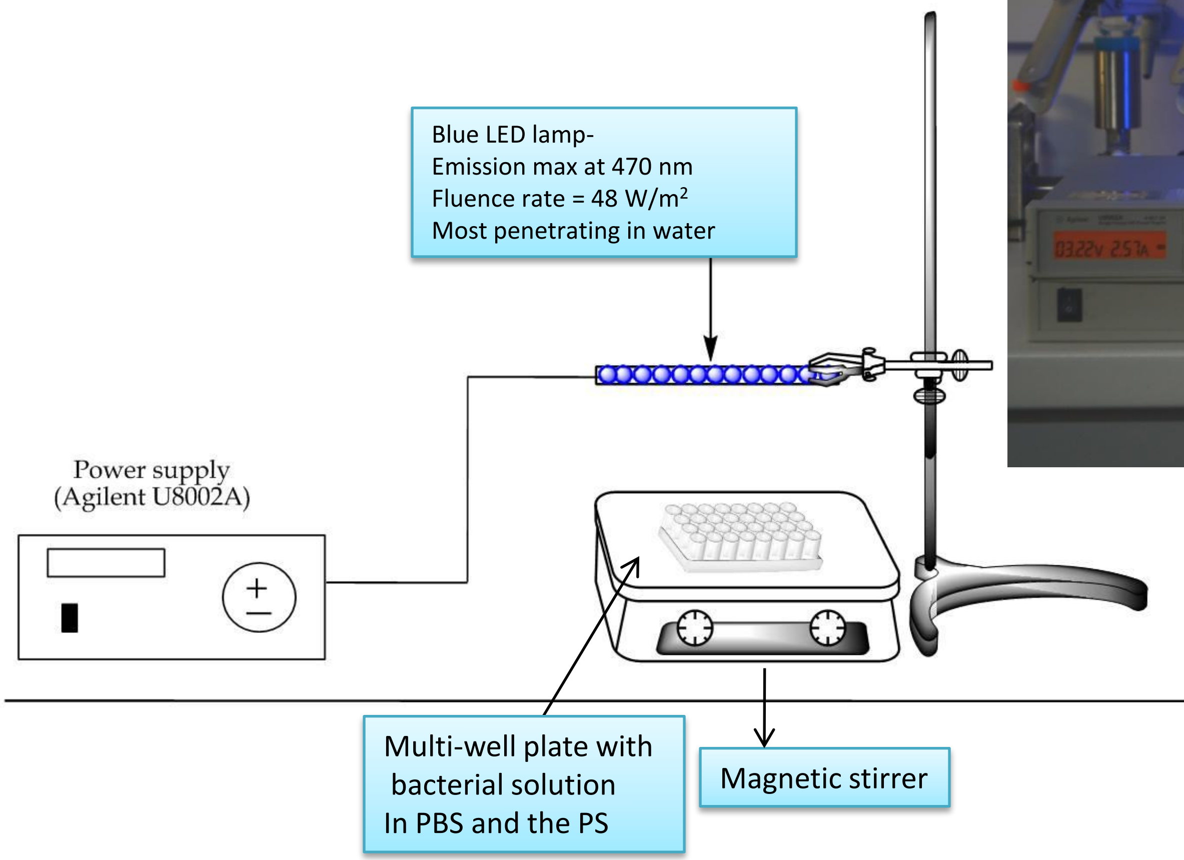


50 µl SPION-TPP in 450 µl

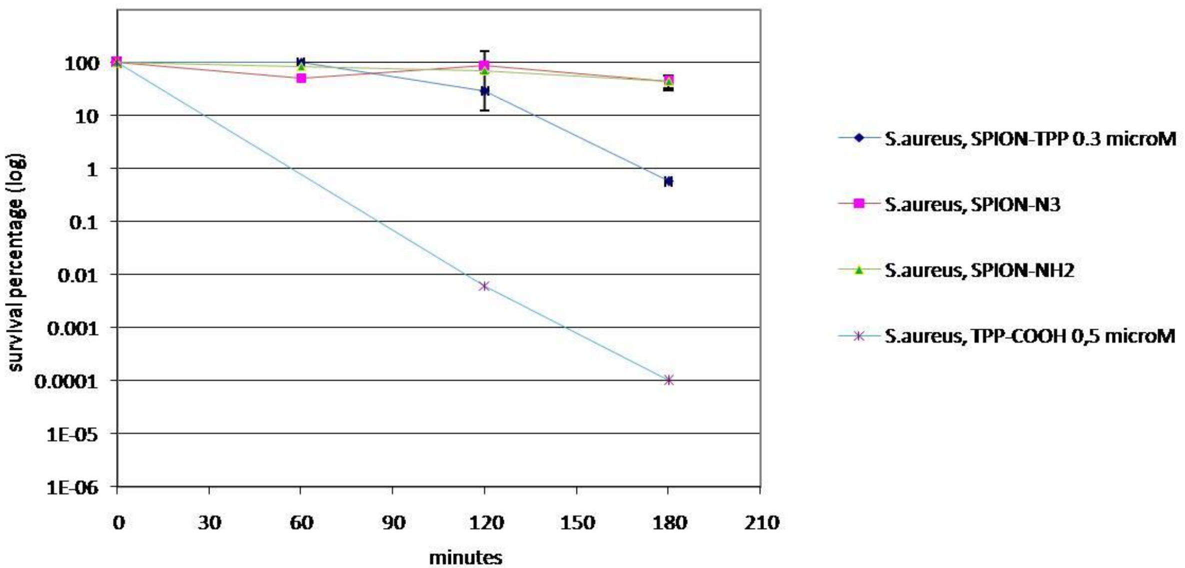
Loading of TPP on SPION calculated = 30 molecules of TPP

Photoxidation setup

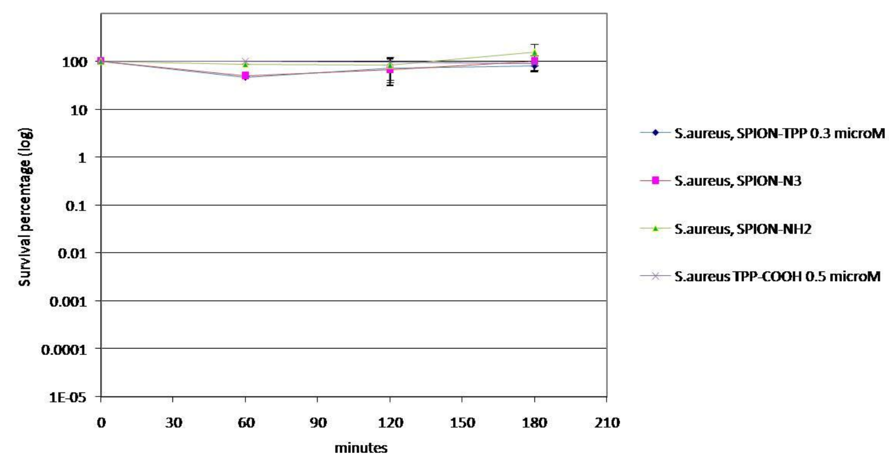
Schematic representation



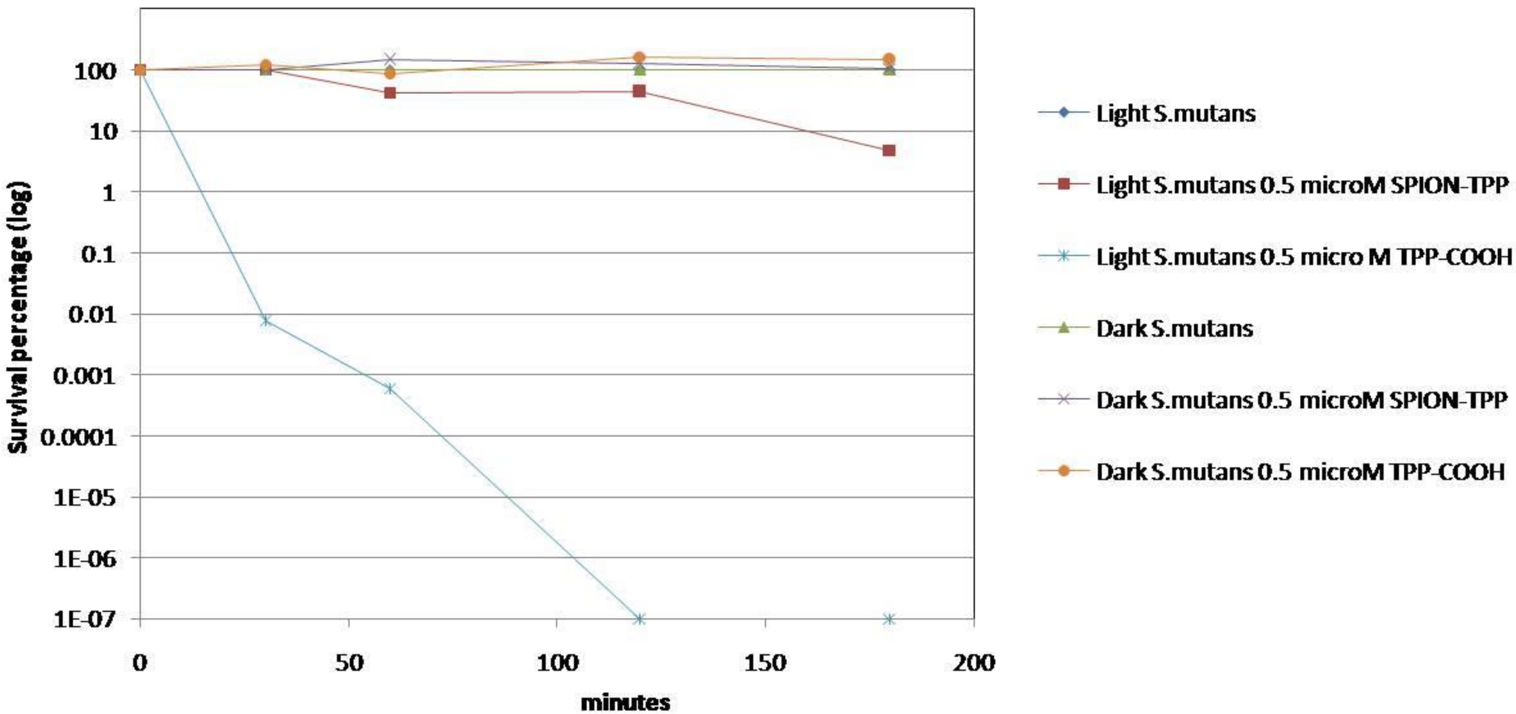
Effect of photosensitized treatment on *S.aureus* with SPION-TPP



Time (min)	Percentage abatement	
PS	120 min	180 min
SPION-TPP (0.3µM)	70.65	99.43
Free TPP-COOH (0.5 µM)	99.99375	99.9999
SPION-NH_2	29.65	54.66
SPION-N_3	9.85	56.23



Photodisinfection of *S.mutans* with SPION-TPP



Percentage abatement of *S.mutans* by the materials

Illumination time (min)	Light, SPION-TPP 0.5 μM	Light, TPP-COOH 0.5 μM	Dark, SPION-TPP 0.5 μM	Dark, TPP-COOH 0.5 μM
60	57.21393 %	99.9994 %	-44.61 %	12.43781 %
120	56.33499 %	100 %	-26.6998 %	-62.1891 %
180	95.10448 %	100 %	-5.63847 %	-46.7662

Polyvinylchloride (PVC) supported photosensitizers

- Why PVC?
  - Low cost polymer and easily available
  - Available in flexible and rigid forms
  - Good chemical resistance
  - Used in various fields of application like electrical, medicine, packaging, protective clothing etc.

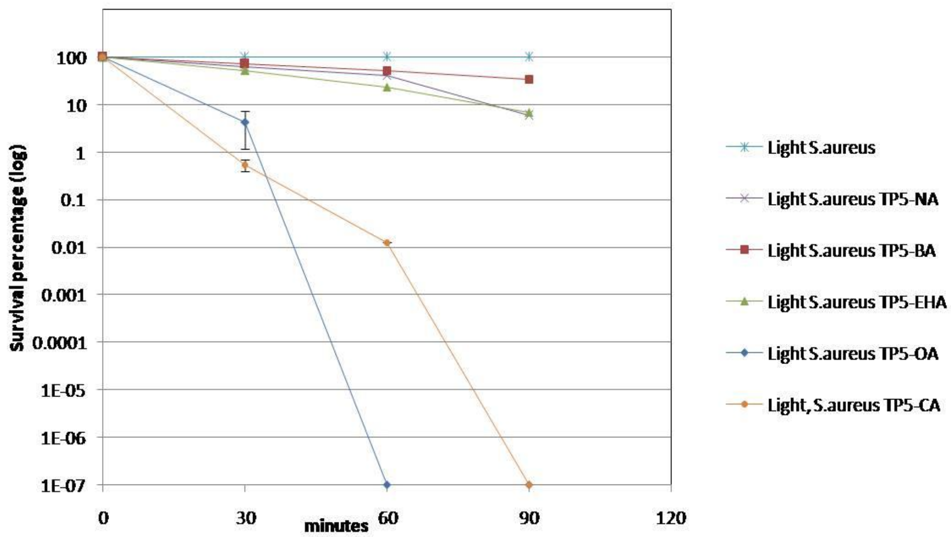
TPP-PVC films prepared using different adipates

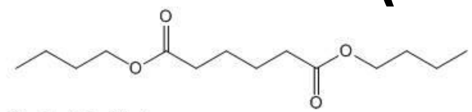
Name	Ingredients (mg)			
	PVC	TPP	Adipate	Film Thickness (µm)
TP5-NA	100	5	00	50
TP5-OA	100	5	19.60 (20 µl)	70
TP5-CA	100	5	20 µl	75
TP5-BA	100	5	19.24 (20 µl)	50
TP5-EHA	100	5	18.60 (20 µl)	65
PVC-NA	100	00	00	50
PVC-OA	100	00	19.60 (20 µl)	70
PVC-BA	100	00	19.24 (20 µl)	55
PVC-EHA	100	00	18.60 (20 µl)	45

NA-no adipate; OA- di n-octyl adipate; BA- di n-butyl adipate; EHA-bis (2-ethyl hexyl) adipate; CA- di capryl adipate

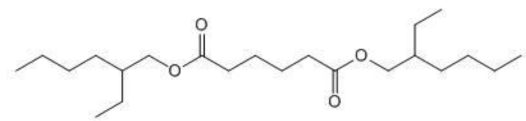
Solvent used: Tetrahydrofuran (THF)

Effect of different adipates on the photo-disinfection ability of TPP-PVC films (*S.aureus*)

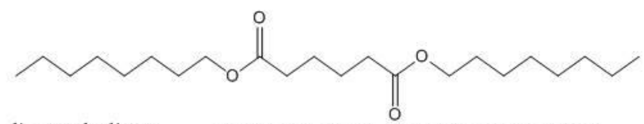




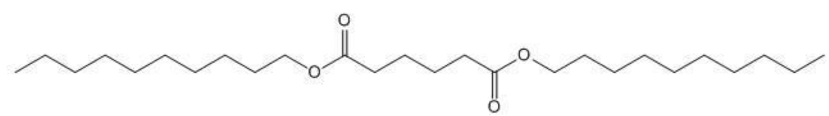
di n-butyl adipate   Chemical Formula: $C_{14}H_{26}O_4$, M. W.= 258.35



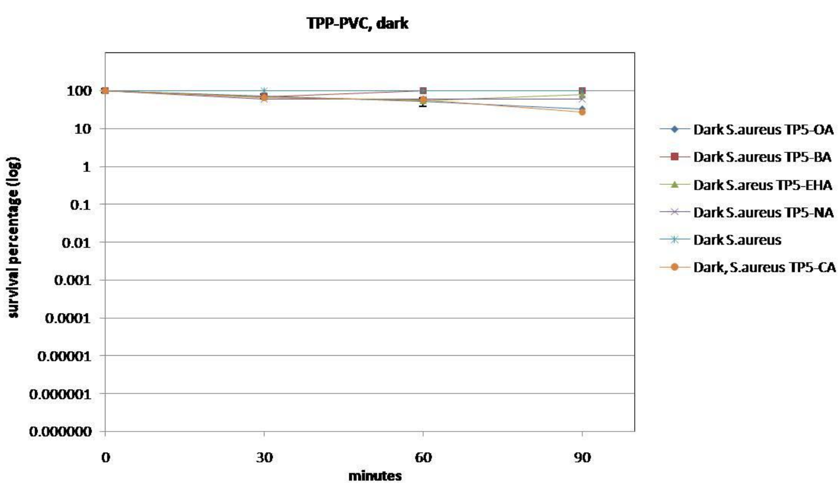
bis (2-ethylhexyl) adipate Chemical formula : $C_{22}H_{42}O_4$, M. W.= 370.57

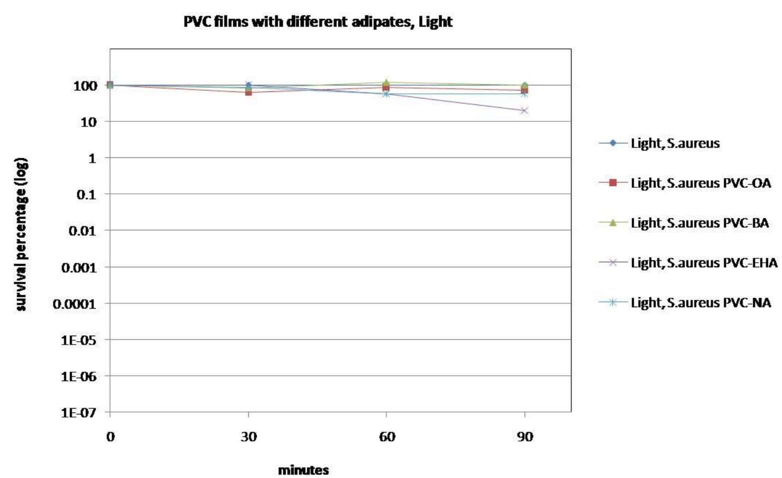


di n-octyl adipate   Chemical formula: $C_{22}H_{42}O_4$,M. W.= 370.57

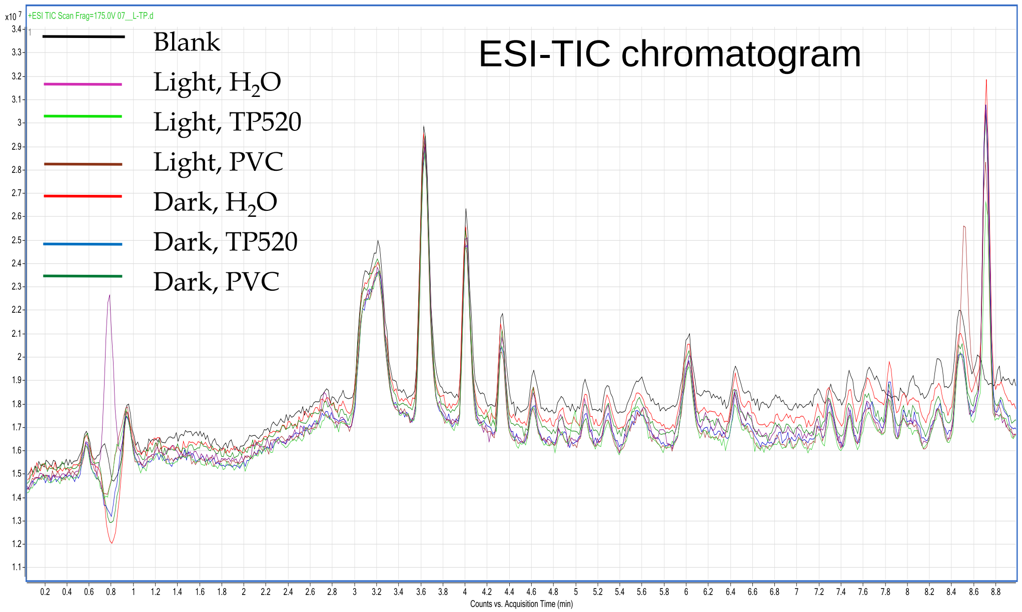


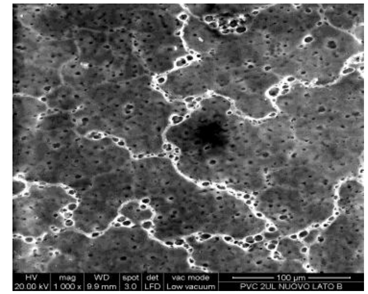
di capryl adipate   Chemical formula:$C_{26}H_{50}O_4$, M.W=426.67



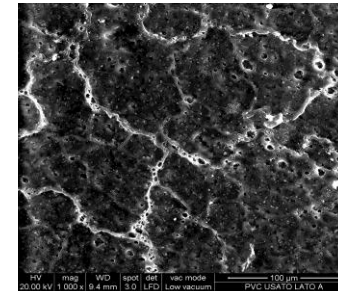


Study of TP520 films before and after illumination

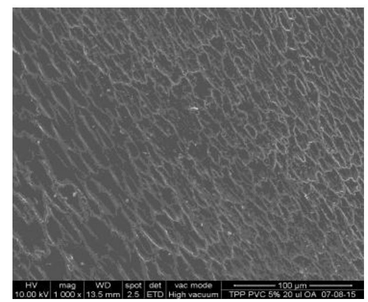




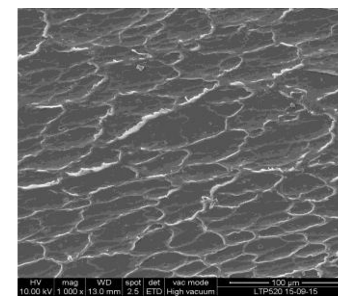
PVC- 20 µl OA



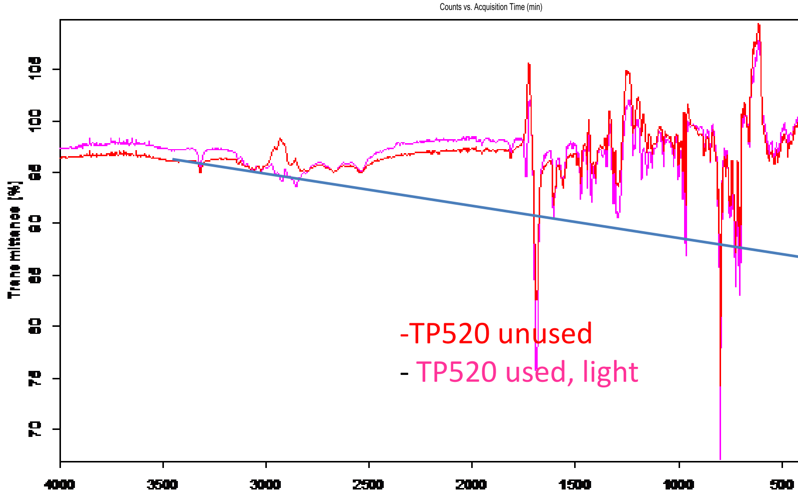
Light, PVC- 20 µl OA



5% TPP-PVC- 20 µl OA



Light, 5% TPP-PVC- 20 µl OA

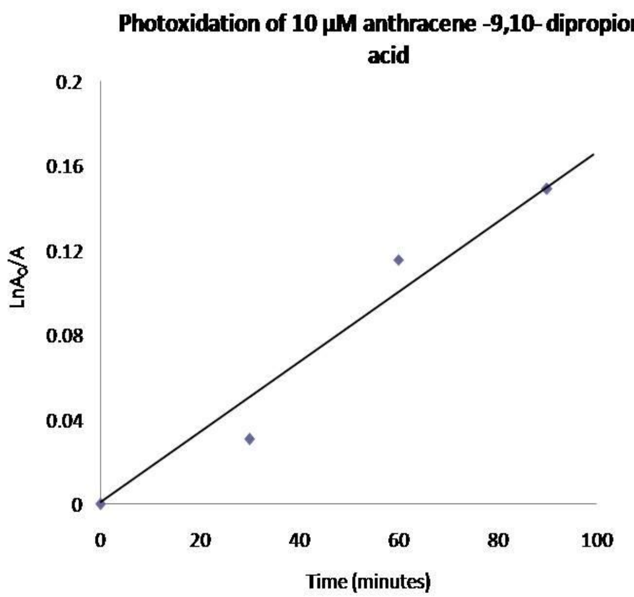


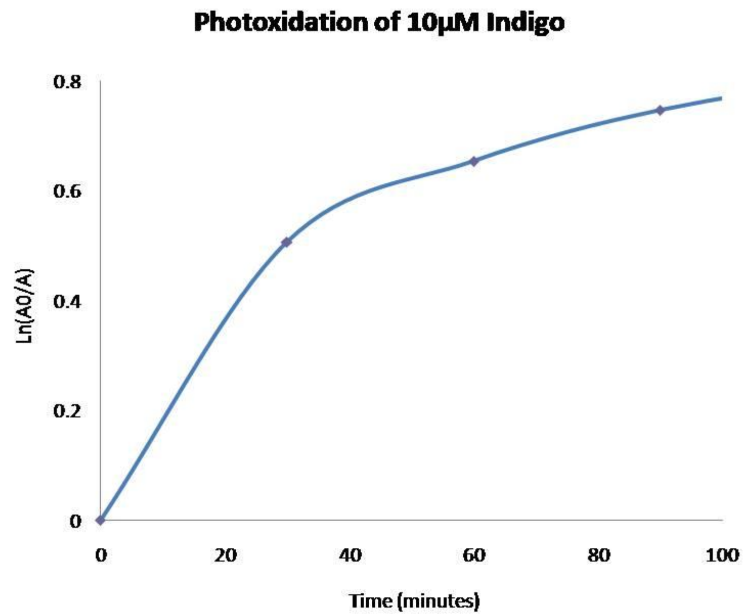
Oxidized PVC -1700 cm^{-1} and 3550 cm^{-1}

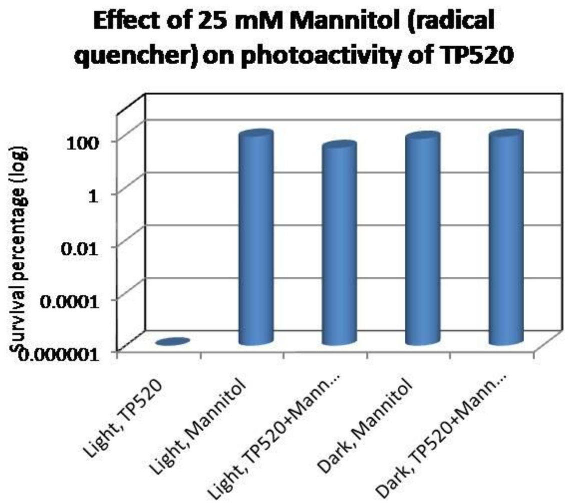
No new peak is observed

C. Decker, Oxidative degradation of Polyvinylchloride, *Journal of Applied Polymer Science*, vol 20, 3321,-3336, 1976

ROS generation

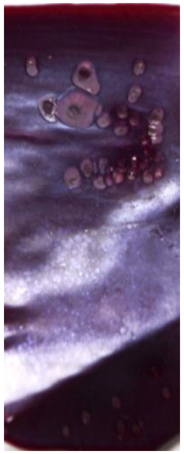




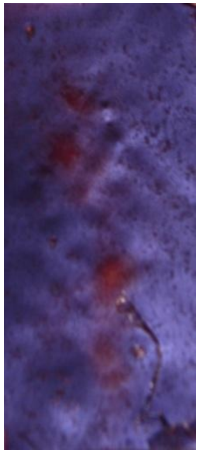


TPP-PVC films with varying concentrations of di n-octyl adipate

Name	Ingredients (mg)			
	PVC	TPP	Adipate	Film Thickness (µm)
TP-520	100	5	19.60 (20 µl)	90
TP-540	100	5	39.20 (40 µl)	70
PVC-20	100	00	19.60 (20 µl)	70

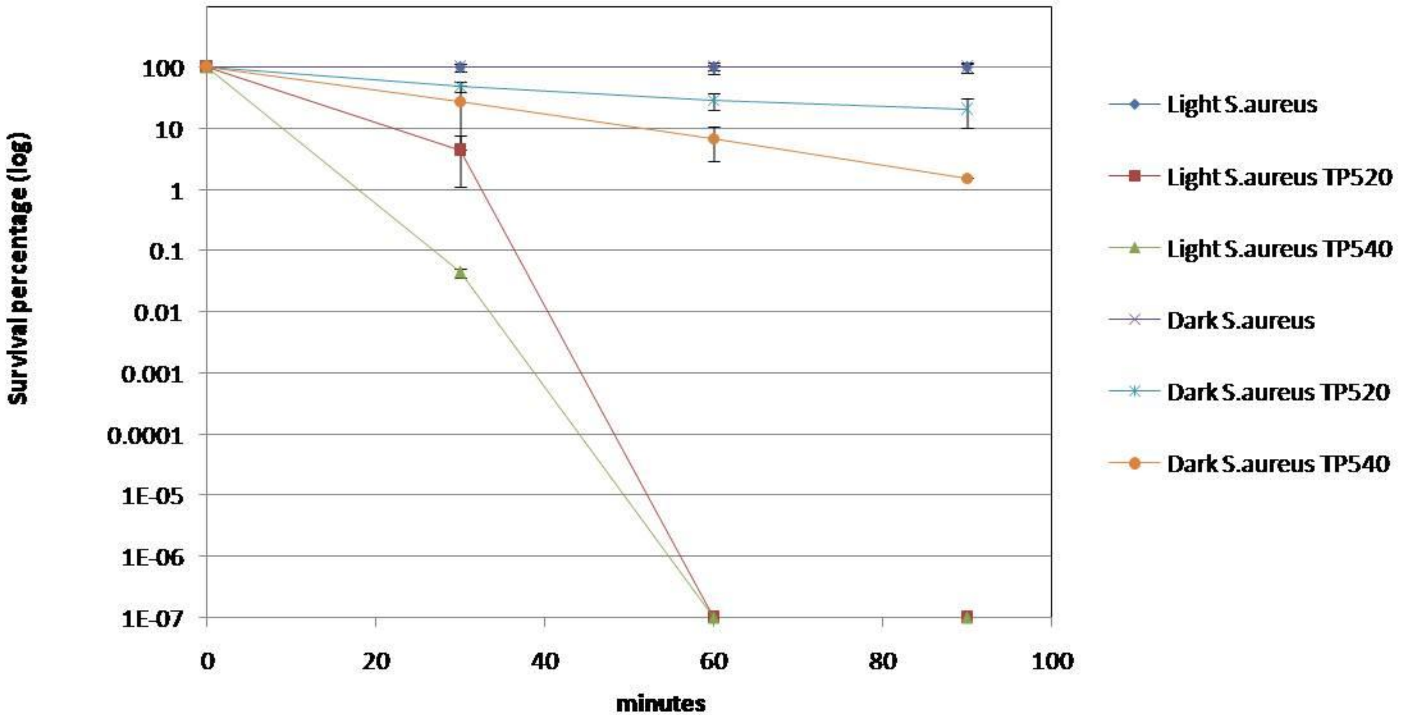


5 % TPP-PVC film with 20 µl OA



5 % TPP-PVC film with 40 µl OA

Effect of different concentrations of di n-octyl adipate on photodestruction of *S.aureus*



Percentage abatement

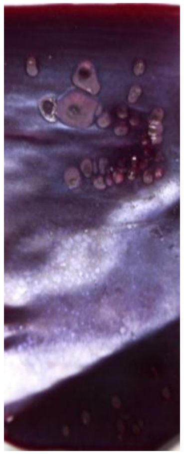
Irradiation time	LTP520	LTP540
30	95.64733 ± 3.2030	99.9552 ± 0.0075
60	100 ± 0	100 ± 0
90	100 ± 0	100 ±0

TPP-PVC films with different concentrations of TPP

Name	Ingredients (mg)			
	PVC	TPP	Adipate	Film Thickness (µm)
TP1-OA	100	1	19.24 (20 µl)	40
TP5-OA	100	5	19.60 (20 µl)	70
PVC-OA	100	00	19.60 (20 µl)	70

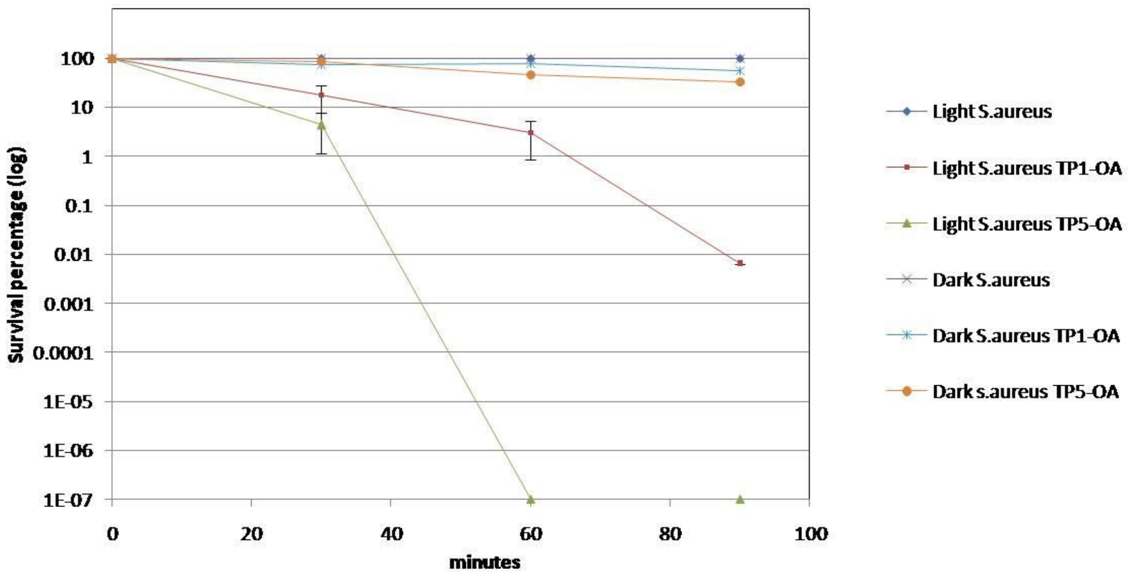
1 % TPP-PVC film with 20 µl OA

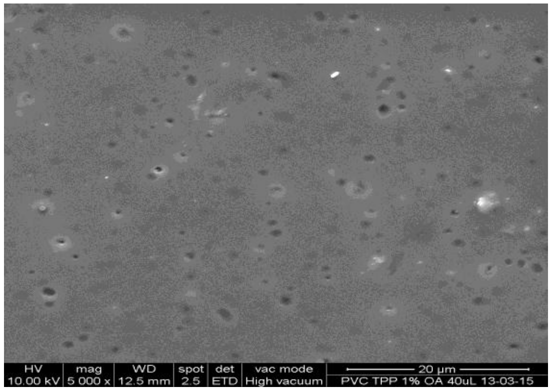
PVC film with 20 µl OA



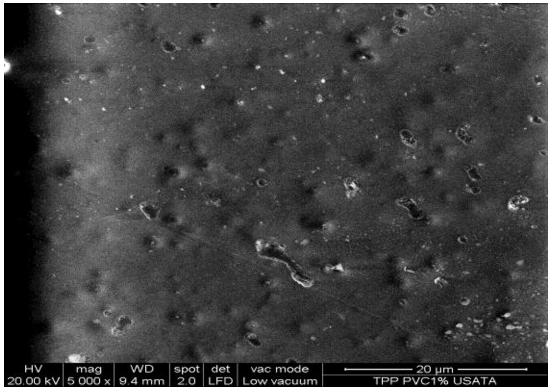
5 % TPP-PVC film with 20 µl OA

PVC films with different concentrations of TPP- Photoefficiency on *S.aureus*





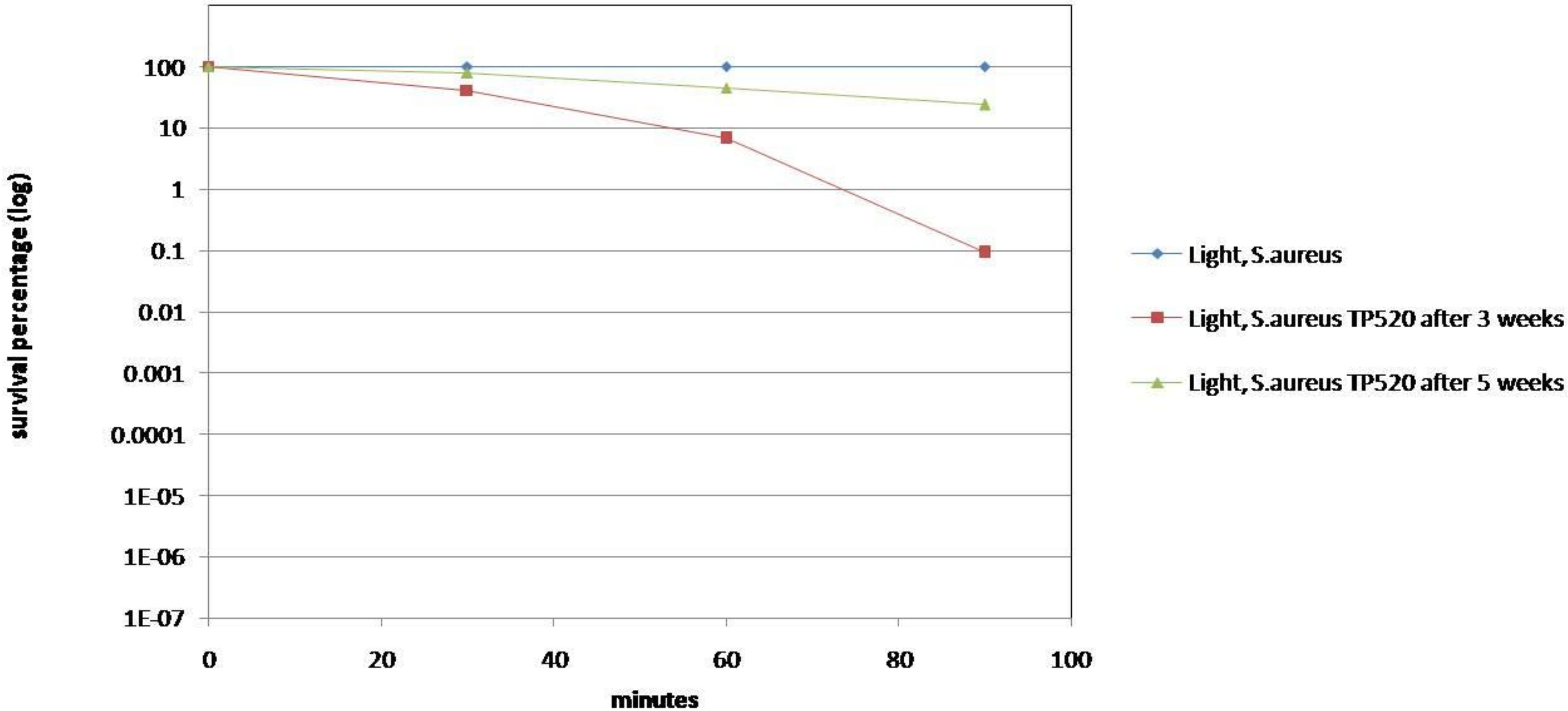
1% TPP-PVC- 20 µl OA



Light, 1% TPP-PVC- 20 µl OA

Irradiation time	LTP1-OA	LTP5-OA
30	82.57528 ± 9.78	95.64733 ± 3.2030
60	96.99165 ± 2.1412	100 ± 0
90	99.99375±0.0069	100 ± 0

Recovery and reuse of TP520 films: phototreatment on



Percentage abatement

Irradiation time	TP520- 3 weeks	TP520- 5 weeks
30	59.32203	21.34831
60	93.33333	54.54545
90	99.90833	76.14035

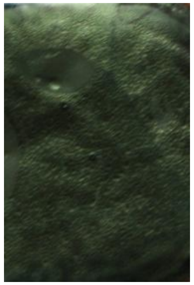
Polyvinylchloride (PVC) supported pentaphyrin (PCCox)

Formulations of PCCox-PVC films

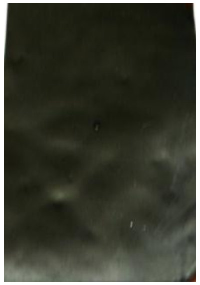
Name	Ingredients (mg)			
	PVC	PCCox	OA	Film thickness (µm)
P-510	100	5	9.5 (10 µl)	75
P-520	100	5	19.60 (20 µl)	60
P-540	100	5	39.20 (40 µl)	70

Solvent used : Tetrahydrofuran (THF)

5% PCCox-PVC with 10µl OA

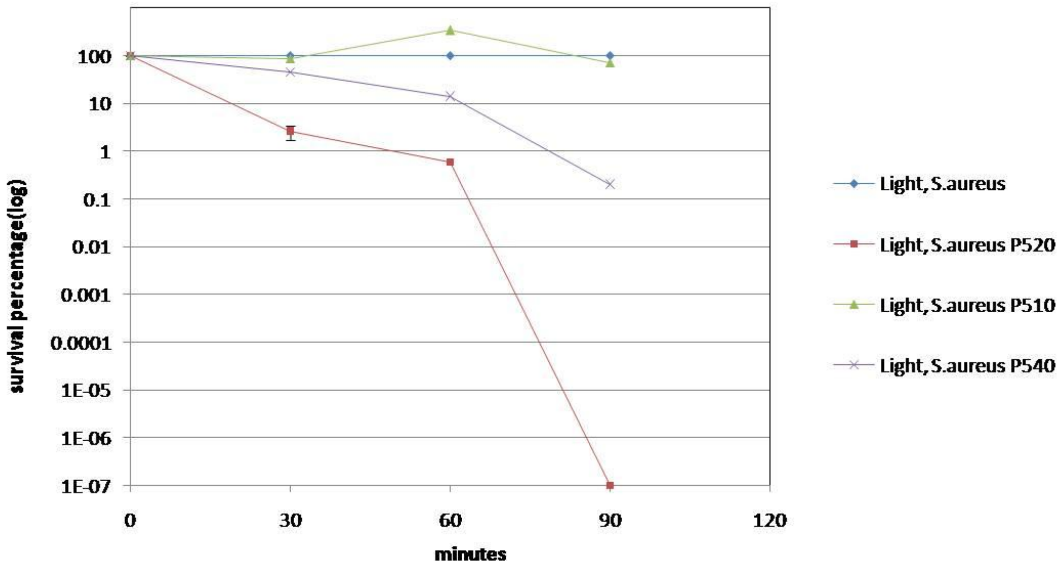


5% PCCox-PVC with 20µl OA

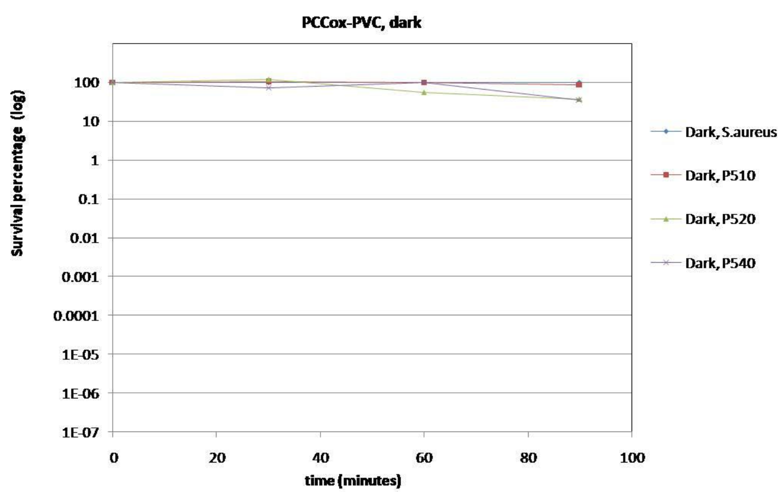


5% PCCox-PVC with 40µl OA

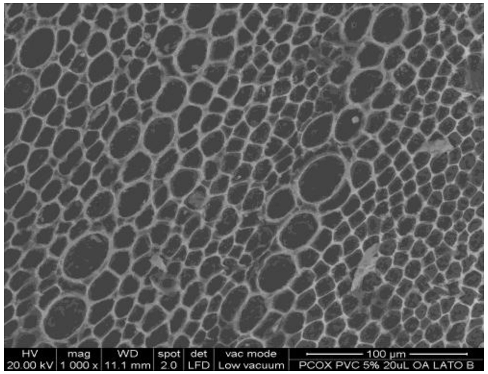
Photodisinfection efficiencies of PCCox-PVC films on *S.aureus*



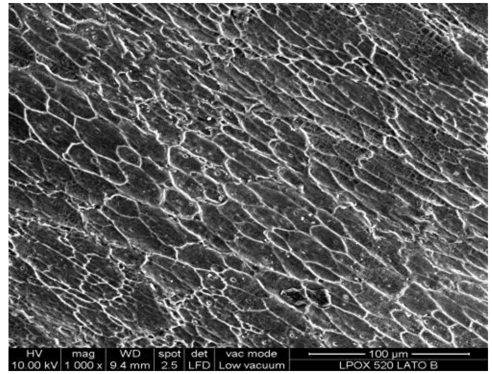
Time (min)	Percentage abatement		
PS	30 min	60 min	90 min
LP-510	11.8024	-236.875	27.6020
LP-520	97.4605	99.4103	100
LP-540	76.2484	86.6984	99.783



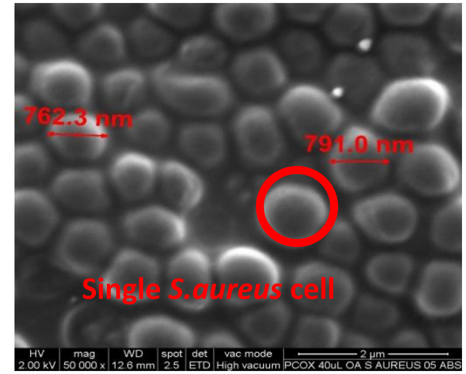
SEM micrographs



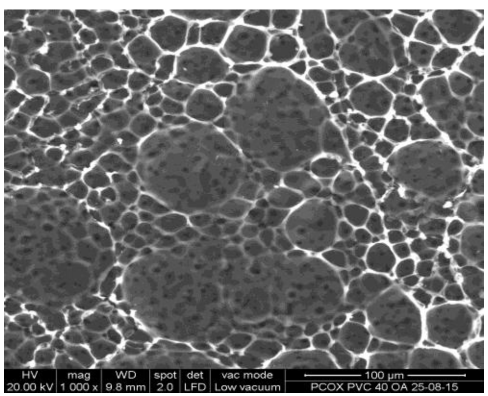
5% PCCox-PVC 20 µl OA



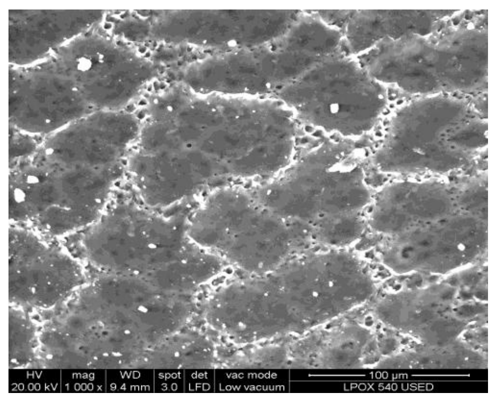
Light, 5% PCCox-PVC 20 µl OA



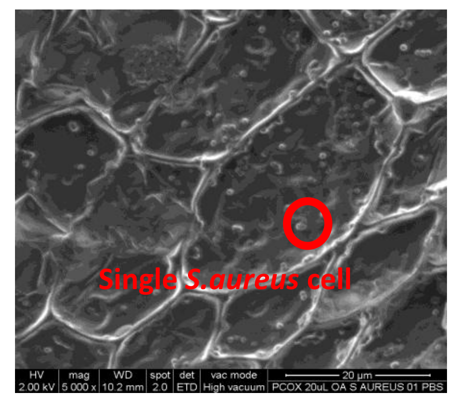
5%PCCox-PVC film with *S.aureus* cells
X 50000 magnification
Absorbance at 600 nm = 0.5



5% PCCox-PVC 40 µl OA

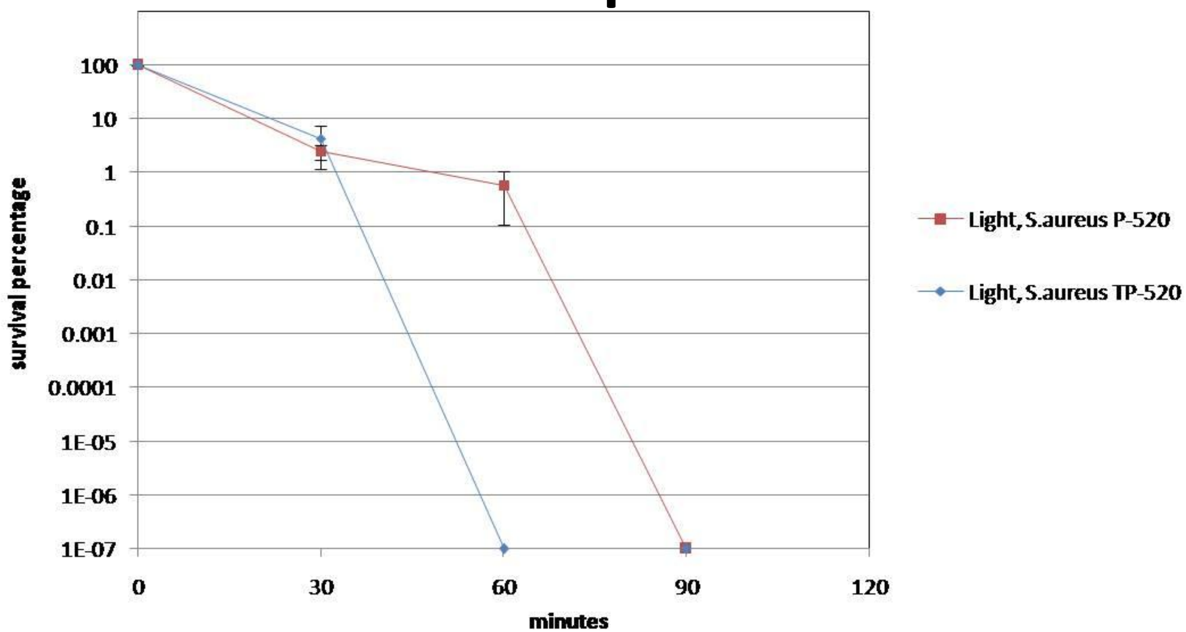


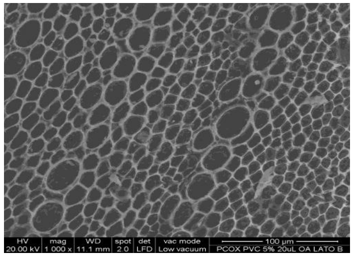
Light, 5% PCCox-PVC 40 µl OA



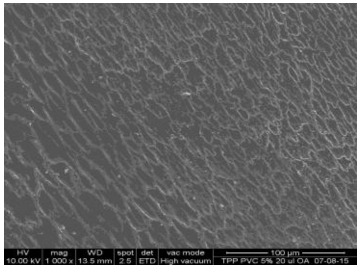
5%PCCox-PVC film with *S.aureus* cells
X 5000 magnification
Absorbance at 600 nm = 0.1

PCCox-PVC and TPP-PVC-comparison of photo efficiencies





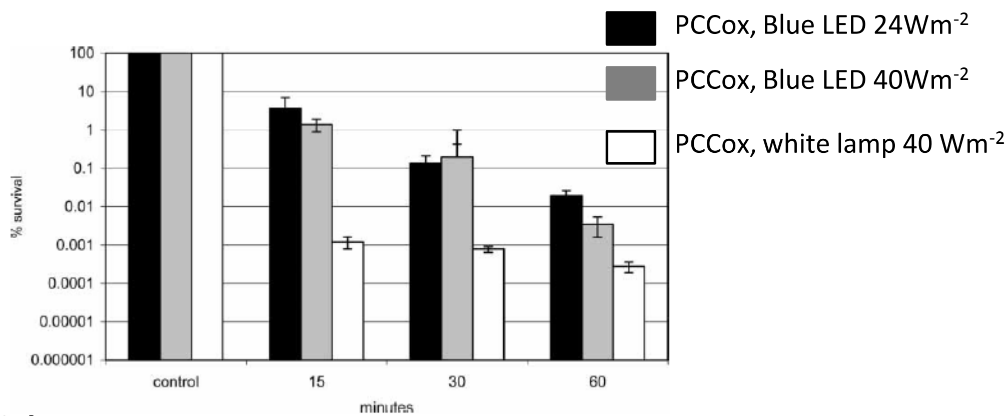
5% PCCox-PVC 20 µl OA



5% TPP-PVC- 20 µl OA

Time (min)	Percentage abatement	
	PCCox	TPP-COOH
15	98.613	99.683
30	99.865	99.952
60	99.981	99.995

Effect of PCCox and TPP-COOH on *S.aureus* under white light



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Conclusions

- Syntheses of expanded porphyrins revealed that meso substituted pentaphyrins are less stable and were not obtained in pure and isolated form
- Use of magnetic supports to immobilize photosensitizers are promising
- Immobilization of TPP and PCCox on PVC proved successful with significant photoactivity at a concentration of 5%
  - Recovery of these films is very simple
  - The films have lesser activity during reuse but the activity can be enhanced by reinforcing the films which can be done by redissolving and recasting the films in suitable solvent

Acknowledgements

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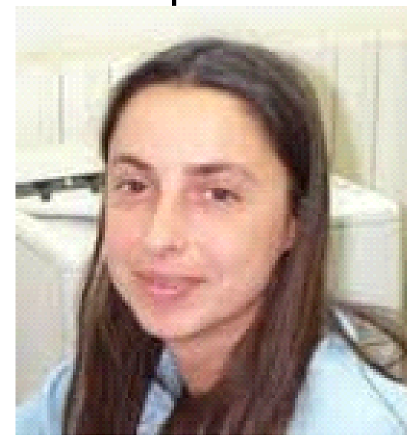
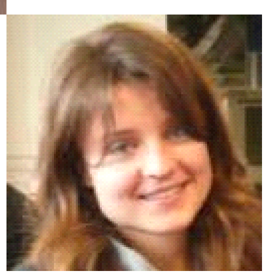
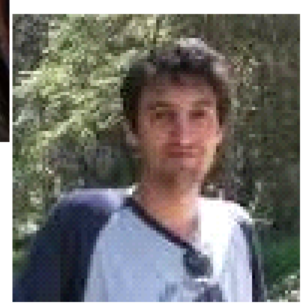
Prof. Daniele Goi

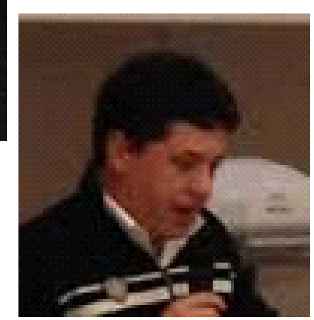
Co-supervisor



Dr. Clara Comuzzi







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Thank you
for your patience
and kind attention!