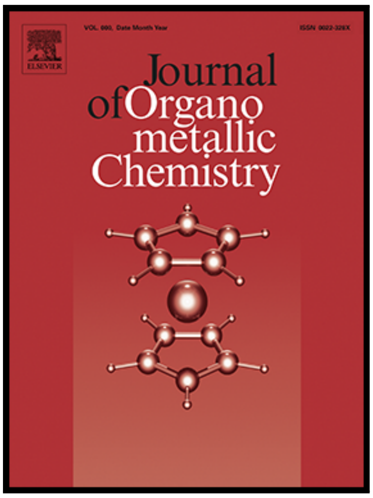

Partial and Full β-Bromination of meso-Tetraphenylporphyrin: Effects on the Catalytic Activity of the Manganese and Nickel Complexes for photo oxidation of styrene in the presence of molecular oxygen and visible light

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Highlights

- A series of β-brominated *meso*-tetraphenylporphyrins, H_2TPPBr_x (x = 0, 4, 8) have been synthesized and the photocatalytic activity of their manganese (III) and nickel (II) complexes in photo oxidation of styrene was thoroughly investigated.
- A new green method was developed for photocatalytic oxidation of styrene, using molecular oxygen in the presence of visible light.
- UV-VIS and ^{1}H- NMR techniques were used to characterize the synthesized catalysts.
- The effect of solvent and bromination degree was studied on the catalytic activity and stability of sensitizers.
- The effect of bromination on the stability of synthesized catalysts and their photocatalytic oxidation was examined.

Partial and Full β-Bromination of *meso*-Tetraphenylporphyrin: Effects on the Catalytic Activity of the Manganese and Nickel Complexes for photo oxidation of styrene in the presence of molecular oxygen and visible light

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Abstract

A series of β-brominated *meso*-tetraphenylporphyrins, H_2TPPBr_x (x = 0, 4, 8) have been synthesized and the photocatalytic activity of their manganese (III) and nickel (II) complexes in photo oxidation of styrene was thoroughly investigated. The green photo oxidation process was done using molecular oxygen and in the presence of visible light. The effect of solvent and bromination degree was studied on the catalytic activity and stability of sensitizers. Based on the obtained results, free base porphyrins showed better catalytic activity among metallated counterparts and the order of catalytic activity was as follows: $H_2TPPBr_4 > H_2TPPBr_8 > H_2TPP$. The order for Ni and Mn metallated porphyrins was also obtained as: $NiTPPBr_8 > NiTPPBr_4 > NiTPP$ and $MnTPPBr_4(OAc) > MnTPP(OAc) >>> MnTPPBr_8(OAc)$, respectively. According to the stability studies, significant increase was observed after addition of metal in porphyrin structure; i.e. more than 80% in the case of Ni. Finally, a mechanism was proposed for photo oxidation of styrene in the presence of H_2TPP porphyrin.

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Keywords: *β-brominated porphyrins, Photo oxidation, Styrene, molecular oxygen*

1. Introduction

Porphyrins, which are characterized by a large number of electrons extended over the macromolecule have been widely studied in the past two decades. Nonlinear optical properties as well as possible applications in photosynthesis, transport and storage of oxygen, electron transfer and biomedical applications bring them to the center of attentions [1-8]. Various functionalized porphyrins are prepared by regioselective substitution of *meso* or *beta* carbon atom positions [9-11]. One of the most exploited porphyrins is *meso*-tetraphenylporphyrin prepared by substitution of phenyl groups in the *meso*-positions with versatile applications in medicine, electronics and optics [12-15]. The physicochemical properties of *meso*-tetraphenylporphyrins are highly sensitive to introduction of any substituent (e.g. bromination, chlorination, nitration and etc.) in *beta*-positions. In this regard, there have been an interest for designing different brominated *meso*-tetraphenylporphyrin as well as their metalloporphyrins complexes especially due to the electron-withdrawing nature of final macrocycle, which is desirable for catalytic applications.

Catalytic activity of *meso*-tetraphenylporphyrins in oxidation reactions has been widely studied during the past decade. Oxidation reactions of alkyl benzenes, cycloalkanes, olefins, alcohols and ketones are the most endeavored reactions. For instance, Shalit et. al [16] designed an iron meso-tetraphenylporphyrin chloride (Fe[TPP]Cl) complex as a selective catalyst for oxidative cross-coupling of phenols. Halogenated meso-tetraphenylporphyrin Mn(III) complexes were also used as an efficient catalyst for synthesis of polycarbonates and cyclic carbonates [17]. Nickel(II) tetraphenylporphyrin was also acted as an efficient photocatalyst for maleimide annulation reactions. According to the observed results, the performance was superior compared to the metal-based photocatalysts in terms of ready availability and excited state redox properties [18]. Metalloporphyrins has been used for the treatment of cancer and dermatological disease through phoyodynamic therapy (PDT), and advanced materials for engineering molecular antenna for harvesting solar energy [19]. Despite the great potential of metalloporphyrins complexes as catalyst, the major concern of the community is avoiding the use of pollutant co-oxidants or co-catalyst. The need of maintainable advancement in compound industry has persistently caused to notice discover safe, natural agreeable and atom-economic compound procedures, Thereafter, there is a huge demand for green oxidants in catalytic oxidation reactions. Among the mostly common used oxygen donors (e.g. hydrogen peroxide, alkyl peroxides, sodium hypochlorite and oxygen), the molecular oxygen is, definitely, the most attractive mainly due to its abundance and easy handling [20, 21, 22]. Also researches have proposed utilizing engineered polymers as an option because of their wide synthetic assorted variety and generally straight forward control. There is a report of new approach to plan arrangement controlled and stereospecific oligomers chain development and successive photoinduced RAFT single unit monomer inclusion (Photograph –RAFT SUMI). [23]

In this study, a new green method was developed for photocatalytic oxidation of styrene using β-brominated *meso*-tetraphenylporphyrins. Molecular oxygen in the presence of visible light was used to study the catalytic activity of manganese(III) and nickel(II) complexes of β-brominated *meso*-tetraphenylporphyrins, H_2TPPBr_x (x =0, 4, 8), in photo oxidation of styrene. The effect of bromination on the stability of synthesized catalysts and their photocatalytic oxidation was examined.

2. EXPERIMENTAL

2.1. Materials and methods

Bruker FT-NMR 300 (300 MHz) spectrometer was used for ^{1}H NMR spectroscopy in $CDCl_3$ solution (see Table1 and Table 2). The remaining $CHCl_3$ in conventional 99.8 atom% $CDCl_3$ creates a signal at d = 7.26 ppm, which was utilized for the calibration of the chemical shift scale. The electronic absorption spectra were recorded on a single beam spectrophotometer (Camspect, UV-M330) in CH_2Cl_2, EtOH or DMF. Gas chromatographic analyses were performed on Agilent Technologies GC-7890B flame ionization detector (FID) with a HB-5 capillary column.

Table 1. The 1H NMR data of H_2TPPBr_x (x= 0,4,8)

Porphyrins	ß-Pyrrole (ppm)	o-Phenyl (ppm)	m,p-Phenyl (ppm)	N-H (ppm)
H_2TPP	8.85 (s,8H)	8.20-8.24 (m,8H)	7.73-7.77 (m,12H)	-2.77 (s,2H)
H_2TPPBr_4	8.69 (s,4H)	8.16-8.19 (m,8H)	7.70-7.90 (m,12H)	-2.82 (s,2H)
H_2TPPBr_8	----	8.13-8.15 (m,8H)	7.72-7.75 (m,12H)	-1.25 (broad,2H)

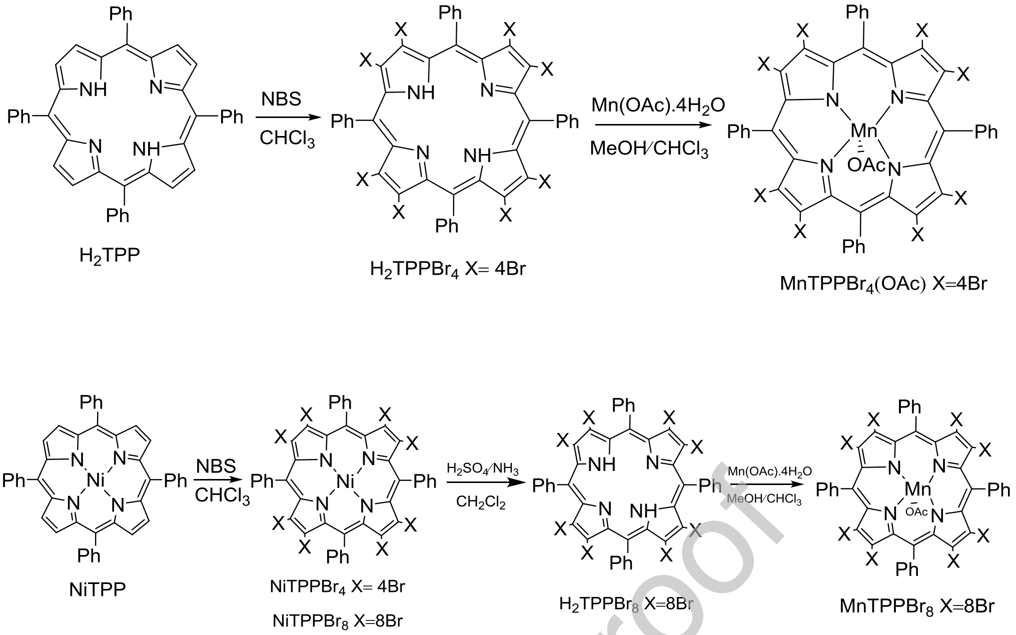
Table 2. The 1H NMR data of NiTPPBr$_x$ (x= 0,4,8)

Porphyrins	ß-Pyrrole (ppm)	o-Phenyl (ppm)	m,p-Phenyl (ppm)	N-H (ppm)
NiTPP	8.74 (s,8H)	8.13-8.20 (m,8H)	7.73-7.77 (broad,12H)	----
NiTPPBr4	8.54-8.85 (s,4H)	8.18-8.37 (m,8H)	7.65-7.91 (m,12H)	----
NiTPPBr8	----	8.00-8.10 (m,8H)	7.75-7.90 (m,12H)	----

All of the chemicals and solvents were purchased from Merck Company and were employed without extra purification.

2.1. Synthesis

A schematic for preparation of brominated porphyrins and metalloporphyrins can be seen in Scheme1.



Scheme1. Preparation of brominated porphyrins and metalloporphyrins.

Synthesis procedures of porphyrins and metalloporphyrins are as follow:

2.2.1. H_2TPP

Freshly distilled pyrrole (2.58 ml, 37 mmole) and benzaldehyde (3.87 ml, 37 mmole) are added to 25 ml of refluxing propionic acid. After refluxing for 90 minutes, the solution is cooled to room temperature and filtered and the filter cake is washed with methanol and hot water. The resulting purple crystals are air dried and finally dried in vacuum oven.

2.2.2. H_2TPPBr_x (x = 2, 4)

First 250 mgr (0.4 mmole) H_2TPP was dissolved in 20 ml of chloroform. Then 144 mgr (0.8 mmole) of freshly crystallized N-bromosuccinimide (NBS) was added to this solution. The reaction left stirring for 24 hrs. The formation of Soret band at 423 nm is the indication of H_2TPPBr_2 formation (see Table 3). For the synthesis of H_2TPPBr_4, 250 mgr (0.4 mmole) H_2TPP was dissolved in 20 ml of chloroform. Then 288 mgr (1.6 mmole) of freshly crystallized NBS was added to this solution. The reaction left stirring for 24 hrs. The formation of Soret band at 436 nm is the indication of H_2TPPBr_4 formation.

Table 3. The soret and Q (0,0) bands of H2TPPBr$_x$ (x= 0,4,8) in comparison with the bands of H$_2$TPP

Porphyrins	Soret band λ(nm)	Q(0,0) band λ(nm)
H_2TPP	418	646
H_2TPPBr_4	440	683
$\Delta\tilde{\nu}$ (cm^{-1})^{a}	1196	838
H_2TPPBr_8	469	745
$\Delta\tilde{\nu}$ (cm^{-1})	2601	2057

$^{a}\Delta\tilde{\nu}= 10^{7}\ ({}^{1}/_{\lambda_1} - {}^{1}/_{\lambda_2})$ relative to the corresponding band of H_2TPP

2.2.3. NiTPP

First 0.3 gr (0.3 mmole) of pure H_2TPP was added to 20 ml of refluxing dimethylformamide (DMF). Then, 0.8 gr (3 mmole) Ni(OAc)$_2$.4H_2O) was added to the solution and kept refluxing for 2 hrs.

2.2.4. NiTPPBr$_x$ (x = 2, 4, 6, 8)

0.13 gr (0.13 mmole) NiTPP was dissolved in 20 ml chloroform and 0.07 gr (0.4 mmole) of freshly crystallized NBS was added to the solution. The reaction left stirring for 24 hrs. The formation of Soret band at 424 nm is the indication of NiTPPBr$_2$ formation. For the synthesis of NiTPPBr$_4$, 0.13 gr (0.13 mmole) NiTPP was dissolved in 20 ml chloroform and 0.14 gr (0.8 mmole) of freshly crystallized NBS was added to the solution. The reaction left stirring for 24 hrs. The formation of Soret band at 428 nm is the indication of NiTPPBr$_4$ formation. For the synthesis of NiTPPBr$_6$, a solution containing 1.0 gr (1.5 mmole) NiTPP was prepared in 60 ml 1,2-dichlrobenzene and 1.58 gr (9.0 mmole) freshly crystallized NBS was added to this solution and left refluxing for 3-4 hrs. Shifting of Soret band from 414 nm to 440 nm is the indication for NiTPPBr$_6$ formation (see Table 4). For the synthesis of NiTPPBr$_8$, a solution containing 1.0 gr (1.5 mmole) NiTPP was prepared in 60 ml 1,2-dichlrobenzene and 3.20 gr (18.0 mmole) freshly crystallized NBS was added to this solution and left refluxing for 2-3 hrs. Shifting of Soret band from 414 nm to 445 nm is the indication for NiTPPBr$_8$ formation.

Table 4. The soret and Q (0,0) bands of NiTPPBr$_x$ (x= 0,4,8) in comparison with the bands of NiTPP

Porphyrins	Soret band λ(nm)	Q(0,0) band λ(nm)
NiTPP	414	527
NiTPPBr4	428	545
$\Delta\tilde{\nu}$ (cm-1)a	790	626
NiTPPBr8	445	555
$\Delta\tilde{\nu}$ (cm-1)	1682	957

2.2.5. NiTPPBr$_n$ (n = 6, 8)

For demetallization of nickel porphyrins, 400 mgr of Ni(TPPBr$_n$) was dissolved in 100 ml of CH_2Cl_2 and 30 ml of H_2SO_4 (98%) was slowly added to the solution. This solution was kept stirring for 1-2 hrs.

2.2.6. H$_2$TPPBr$_x$ (x = 6, 8)

The same procedure as 2.2.5 was used.

2.2.7. MnTPP(OAc)

1 mmole H$_2$TPP was added to 50 ml of refluxing DMF. Then, 0.8 gr (3 mmole) Mn(OAc)$_2$.4H$_2$O) was added to the solution and kept refluxing for 2 hrs.

2.2.8. MnTPPBr$_X$(OAc) (x= 2, 4, 8)

For x= 2, 4: 0.11 gr (0.13 mmole) H$_2$TPPBr$_2$ was dissolved in 30 ml chloroform and 0.25 gr (1.04 mmole) Mn(OAc)$_2$.4H$_2$O) which was dissolved in minimum amount of methanol was added to the solution and kept refluxing for 2 hrs. For x=

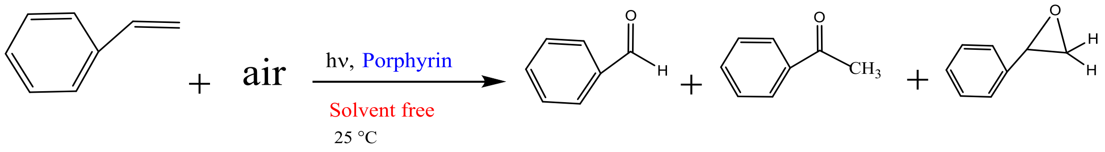
8: 0.02 gr (0.13 mmole) H_2TPPBr_2 was dissolved in 30 ml chloroform and 0.04 gr (0.1 mmole) $Mn(OAc)_2.4H_2O$) which was dissolved in minimum amount of methanol was added to the solution and kept refluxing for 2 hrs (see Table 5).

Table 5. The soret and Q (0,0) bands of MnTPPBrx(OAc) (x= 0,4,8) in comparison with the bands of MnTPP(OAc)

Porphyrins	Soret band λ(nm)	Q(0,0) band λ(nm)
MnTPP(OAc)	479	618
MnTPPBr4(OAc)	488	641
$\Delta\bar{\nu}$ (cm-1)	380	580
MnTPPBr8(OAc)	476	683
$\Delta\bar{\nu}$ (cm-1)	1682	1540

2.2. General oxidation procedure

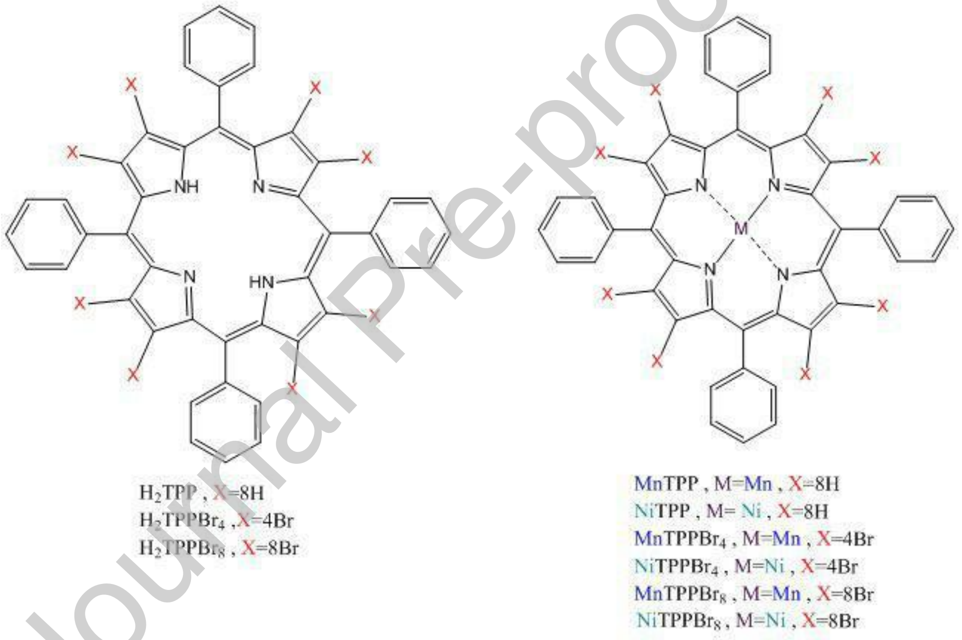
In a model experiment, 2.5× 10^{-6} mole of porphyrins and metalloporphyrins were added to styrene (1× 10^{-2} mole) in a glass tube without any other solvent. Oxygen was bubbled via the solution and the sample was irradiated in the presence of visible light (fluorescent circular lamp, 22 W and 230 V) and ($\lambda > 350$ nm) for 6–72 h at 25 °C; the sample was kept 3 cm from center of the lamp. The products were identified by GC-chromatography. Scheme 2 shows major products of the photo oxidation of styrene that used in this study.



Scheme 2. Photocatalytic oxidation of Styrene by molecular oxygen in the presence of porphyrin or metalloporphyrin sensitizers in solvent free condition at 25 °C

3. Results and discussions

The photocatalytic oxidation of styrene in the presence of porphyrin and metalloporphyrin sensitizers [Mn (III)(TPPBr$_x$)OAc (x = 0, 4 and 8)] and [Ni(II)(TPPBr$_x$) (x = 0, 4, and 8)] were thoroughly studied and compared. In the photocatalytic oxidation process, we used molecular oxygen as a green oxygen donor and studied the degree of bromination on the photocatalytic oxidation of the Mn-porphyrin and Ni-porphyrin. Scheme 3 shows the structures of sensitizers employed in this study.



Scheme3. Free-base (H$_2$TPP, H$_2$TPPBr$_4$ and H$_2$TPPBr$_8$) and their metalated (Mn, and Ni) porphyrins sensitizers.

3.1. The optimal amount of sensitizer

At first, In order to find the optimal conditions for the photo oxidation process, styrene was selected as a model of the alkene family and *meso*-tetra phenylporphyrin (H_2TPP) as a sensitizer was used in different concentrations. The results are presented in Table 6.

Table 6. The effect of different amount of H_2TPP in Photo oxidation of styrene in solvent free condition[a]

Entry	Styrene/ Cat	Cat: H_2TPP	Conversion %	Selectivity % (benzaldehyde)	TON*
1	40000	0.25×10^{-6}	1.3	64	548
2	4000	2.5×10^{-6}	6.66	69	266
3	400	25×10^{-6}	2.33	60	9.32

* Turnover number

[a] Photo oxidation of 0.01 mole styrene by O_2 in the presence of H_2TPP as the photosensitizer under visible light in 24 hrs reaction time

As shown in Table 6, the highest conversion percentage and also the best selectivity for benzaldehyde was obtained in (1/4000) styrene to catalyst ratio. So this ratio was used for all future experiments in the present study.

3.2. The effect of metal in photo oxidation reaction

As mentioned earlier, most porphyrin derivatives in natural environments are metallic porphyrins due to their tunable photochemical properties. In order to study the effect of metal in photo oxidation reaction of styrene, nickel and manganese metals were selected. The photo oxidation reaction of styrene in the presence of metallic porphyrins was carried out using visible light in free solvent conditions within 72 hrs. The results are presented in Table 7.

Table 7. The effect of metal in Photo oxidation of styrene in optimal concentration in solvent free condition[a]

Entry	Catalyst	Conversion %	Selectivity% (benzaldehyde)	TON
1	H_2TPP	4.03 (3.08)[b]	67(79)	161(123)
2	NiTPP	1.34	72	53
3	MnTPP(OAc)	2.28	57	91

[a] Sensitizers (2.5× 10^{-6} mole), styrene (0.01 mol and sub/cat = 4000) in 72 hrs reaction time.

[b] Conversion after 48 hrs reaction time.

According to the obtained results, the highest conversion percentage after 72h irradiation was obtained with non-metallic porphyrin (H_2TPP), while NiTPP showed the best selectivity for benzaldehyde. In the case of metallated porphyrins, manganese porphyrin exhibited better activity than nickel-porphyrin. The order of activity of porphyrins in the photo oxidation reaction of styrene in the presence of visible light is as follows: H_2TPP>NiTPP>MnTPP(OAc)

3.3. Effect of bromination degree at the β positions on catalytic properties

It is well known that the halogenated metalloporphyrins are more robust to oxidative degradation and show enhanced catalytic activities compared to their non-halogenated complement [24-26]. The higher metal^{3+}/metal^{2+} reduction potential of these halogenated derivatives is the main motivation for developing plentiful metalloporphyrins with polyhalogen substituents for various catalytic oxidation systems. In order to study the effect of bromination degree on the catalytic activity of H_2TPP and their Mn and Ni metallated porphyrins, photo oxidation of styrene was carried out in the presence of visible light and under moderate condition of O_2 blubbing. Figure 1 shows the catalytic activity of

H_2TPPBr_x (X= 0, 4, and 8), $MnTPPBr_x(OAc)$ (x = 0, 4, and 8) and $NiTPPBr_x$ (X= 0, 4,and 8) in solvent free condition after 72h irradiation.

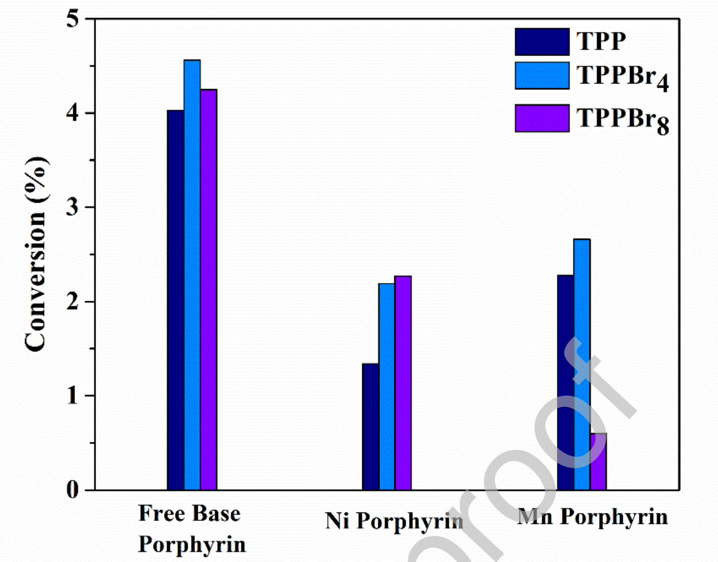


Fig. 1. The effect of the number of bromine atom on the catalytic activity of porphyrins and metalloporphyrins in solvent free condition after 72h irradiation.

Based on the obtained results (Fig.1), the catalytic activity of porphyrin sensitizers was obtained as follows: H_2TPP>MnTPP>NiTPP in solvent free condition. It is worth mentioning that among metallated porphyrins, Mn porphyrins showed better activity than Ni porphyrins.

3.4. Solvent effect

The effect of bromination degree on activity of porphyrins and metalloporphyrins in photo oxidation of styrene was also studied in acetonitrile solvent during 24 hrs and 48 hrs. The results are summarized in Table 8.

Table 8. The effect of bromination degree in photo oxidation of styrene using different sensitizers in the presence of acetonitrile as solvent[a].

Entry	Catalyst	Conversion%	Selectivity%(benzaldehyde)	TON
1	H_2TPP	4.74(4.78)[b]	78(52)[c]	189(191)[d]
2	H_2TPPBr_4	0.27(0.65)[b]	53(22)[c]	10(26)[d]
3	H_2TPPBr_8	0.26(0.58)[b]	53(65)[c]	10(23)[d]
4	NiTPP	0.72(1.4)[b]	81(73)[c]	28(56)[d]
5	$NiTPPBr_4$	0.31(0.45)[b]	53(53)[c]	12(18)[d]
6	$NiTPPBr_8$	0.16(0.40)[b]	53(60)[c]	6(16)[d]
7	MnTPP(OAc)	0.14(0.48)[b]	50(57)[c]	5(19)[d]
8	$MnTPPBr_4$(OAc)	0.21(0.24)[b]	55(53)[c]	8(9)[d]
9	$MnTPPBr_8$(OAc)	0.24(0.34)[b]	53(48)[c]	9(13)[d]

[a] Sensitizers (2.5×10^{-6} mole), styrene (0.01 mole and sub/cat = 4000), 24 hrs reaction time.

[b] Conversion after 48h irradiation.

[c] Selectivity after 48h irradiation.

[d] TON after 48 h irradiation.

Based on the obtained results, it is observed that the presence of bromine has a negative effect on the catalytic activity of free base porphyrin sensitizers. In the steady-state conditions of the air and the visible light and in the presence of acetonitrile, the catalytic activity of porphyrin sensitizers was obtained as follow H_2TPP> H_2TPPBr_4>H_2TPPBr_8 while the NiTPP sensitizer showed the highest conversion percentage and the highest selectivity versus benzaldehyde (Table 8, entry 4), bromine had negative effect on Ni(II) porphyrins (Table 8, entries 4, 5 and 6) the catalytic activity of porphyrin sensitizers in the steady-state conditions of the air and the visible light in acetonitrile solvent and the arrangement of porphyrin activity was obtained as follows: NiTPP>$NiTPPBr_4$>$NiTPPBr_8$.

After 48 hours of reaction, MnTPP(OAc) sensitizer showed the highest conversion percentage and the highest selectivity of benzaldehyde among Mn(III) porphyrins and bromine showed positive effect on photo oxidation of styrene (Table 8, entries 7, 8 and 9) as follows:

$MnTPPBr_8$(OAc)>$MnTPPBr_4$(OAc)>MnTPP(OAc)

It is worth mentioning that the obtained results in the presence of solvent, is in consistent with previous studies that solvents may enhance conversion percent in photo oxidation reactions [27-30].

3.5. The stability of porphyrin sensitizers

The effect of metal on the stability of porphyrin sensitizers was investigated by examining UV-Vis spectrum at room temperature and solvent-free conditions. For the stability study, 2.5×10^{-6} mole of porphyrin and metalloporphyrin sensitizer and 0.01 mole of styrene were used. According to the UV-Vis spectrum seen in Fig.2, H_2TPP (Fig2(a)) was degraded 94% after 24 hrs of the photo oxidation reaction while Mn (Fig2(b)) and Ni (Fig2(c)) porphyrins were degraded 23% and 10%, respectively in the same time. Thus significant stability can be obtained by adding metal in porphyrin structure.

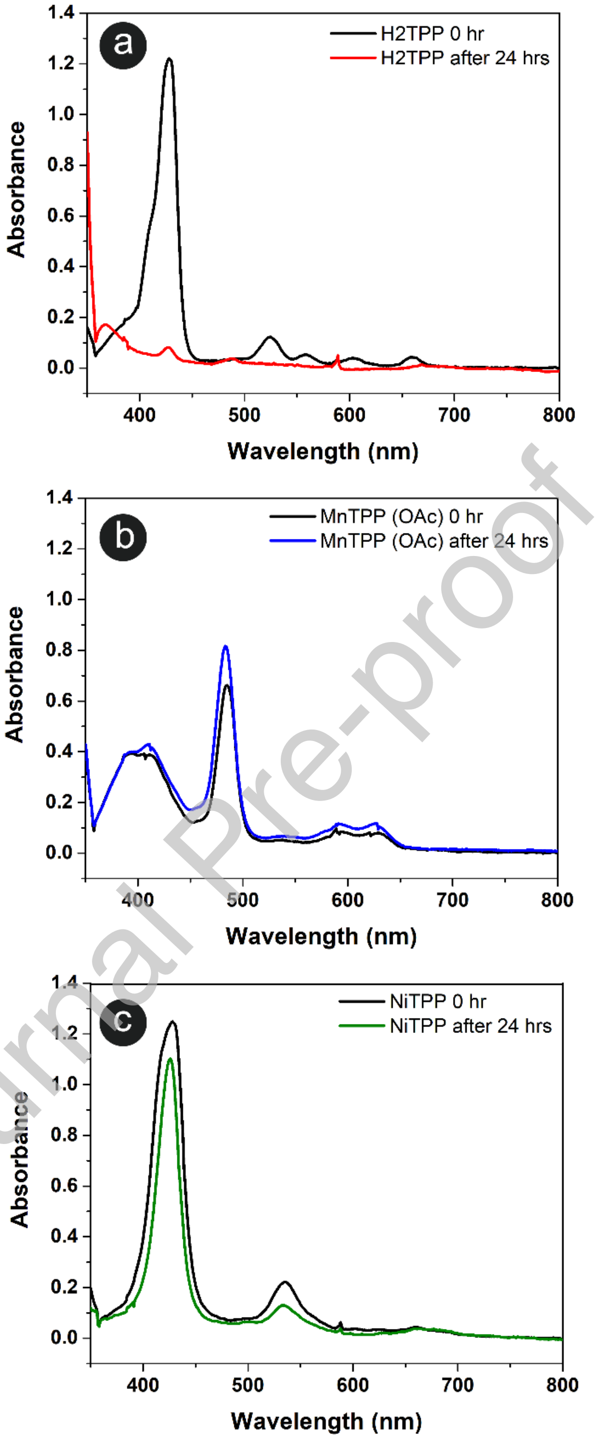


Fig.2 . Stability of porphyrin sensitizers (a) H_2TPP, (b) MnTPP(OAc) and (c) NiTPP after 24 hrs in the solvent free conditions.

3.6. Proposed mechanism for photo oxidation of styrene in the presence of H_2TPP

According to the proposed mechanism Scheme 4, In the absence of metal, the following mechanism can be found when free base porphyrin (H_2TPP) is used as a sensitizer in the reaction of photo oxidation leads to the formation of a single oxygen, which proceeds from another photochemical pathway.

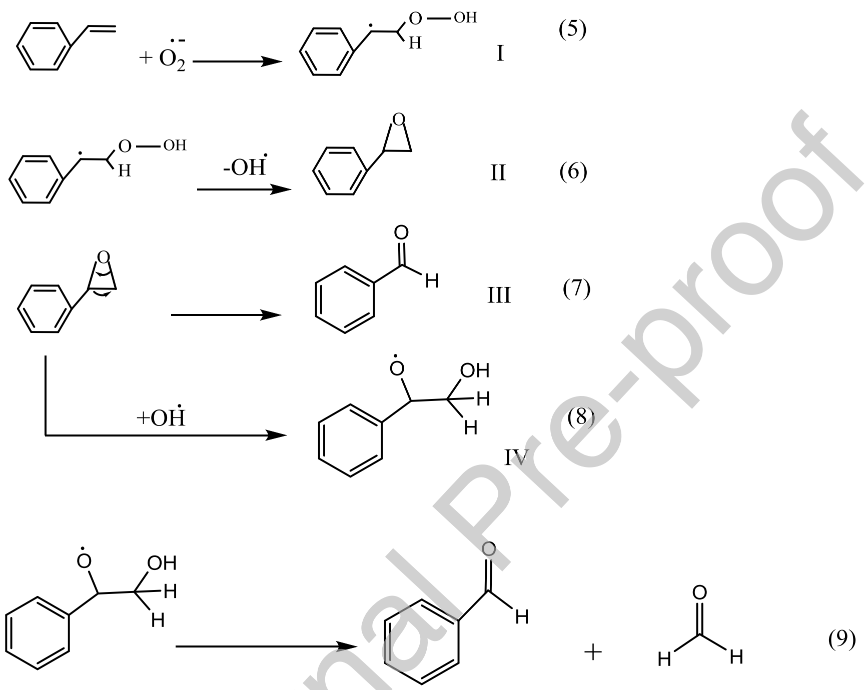
In the first, a photosensitizer is converted to the lowest single-excitation mode by absorbing a certain amount of visible light (^{1}PS*), then follow by intersystem crossing (ISC) sensitizer converted into a triple excited state (^{3}PS*), if energy of this excited state is as large as about 96 kJ/mole, this amount of energy can be absorbed by the oxygen in ground state ($^3\Sigma^-{}_g$) and by the electronic excitation energy transfer (EET) cause formed the lowest excited single oxygen state ($^1\Delta_g$) and the second excited state of oxygen, ($^1\Sigma_g{}^+$). The energy of the singlet state or the triplet state of oxygen is transmitted by photo-induced electron transfer by the light (PET) into the ground state of oxygen($^3\Sigma^-{}_g$), and the molecular oxygen is converted into an anion of superoxide which is a very active radical [31]. Then the anion peroxide enters the CH bond and forms the radical (Scheme4,I) then with loss of the radical OH make epoxide (Scheme4,II), which is highly active, and after an electron transfer, it produces acetophenone. Also, epoxide (Scheme4,II) can absorb radicals from the environment and forming another radical species (Scheme4,III), and then with the breakdown of the bonding and exhaust of formaldehyde, the dominant product (benzaldehyde) is made [32, 33].

$$\mathrm{PS} \xrightarrow{h\nu} {}^{1}\mathrm{PS}^{*} \xrightarrow{\mathrm{ISC}} {}^{3}\mathrm{PS}^{*} \qquad (1)$$

$${}^{3}\mathrm{PS}^{*} + \mathrm{O}_2\ ({}^{3}\Sigma_g^{-}) \xrightarrow{\mathrm{EET}} \mathrm{PS} + \mathrm{O}_2\ ({}^{1}\Delta_g) \qquad (2)$$

$${}^{3}\mathrm{PS}^{*} + \mathrm{O}_2\ ({}^{3}\Sigma_g^{-}) \xrightarrow{\mathrm{EET}} \mathrm{PS} + \mathrm{O}_2\ ({}^{1}\Sigma_g^{+}) \qquad (3)$$

$${}^{3}\mathrm{PS}^{*} + \mathrm{O}_2\ ({}^{3}\Sigma_g^{-}) \xrightarrow{\mathrm{PET}} \mathrm{PS}^{*} + \dot{\mathrm{O}}_2^{-} \qquad (4)$$



Scheme4. Proposed mechanism for photo oxidation of styrene in the presence of H_2TPP porphyrin.

4. Conclusion

We employed a new sort of green, considerably selective, cost effective and photocatalytic method for oxidation of styrene. Air as a clean and accessible oxidant was employed in the presence of visible light irradiation and a series of β-brominated *meso*-tetraphenylporphyrins, H_2TPPBr_x (x = 0, 4, 8) have been synthesized and the catalytic activity of their manganese(III) and nickel(II) complexes were studied for photo oxidation of styrene. Based on the obtained results the free base porphyrins showed superior catalytic activities among metallated porphyrins. In addition, the bromination degree not only played a significant role in catalytic activity of synthesized porphyrins but also enhanced the stability of catalyst up to 8 times.

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