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A novel porphyrinic photosensitizer based on the molecular complex of meso-tetraphenylporphyrin with 2,3-dichloro-5,6dicyano-1,4-benzoquinone: Higher photocatalytic activity, photooxidative stability and solubility in non-chlorinated solvents

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**Abstract**: In order to overcome problems associated with the use porphyrins under photooxidative conditions, the 1:2 molecular complex of meso-tetraphenylporphyrin (H<sub>2</sub>TPP) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) has been used as photosensitizer for the aerobic photooxidation of olefins. Under the optimized conditions, H<sub>2</sub>TPP(DDQ)<sub>2</sub> showed a significantly increased catalytic activity and oxidative stability compared to that of the free base porphyrin. Interestingly, <sup>1</sup>H NMR and UV-vis studies showed that the DDQ molecules efficiently prevent protonation of H<sub>2</sub>TPP under acidic condition formed by exposure of chlorinated solvents to the UV-vis light. The photosensitizing ability of the adduct was found to be mainly dependent on the light absorption in the Soret band region and to a much lesser extent on the absorption in the Q(0,0) band region. Furthermore, substantially increased solubility of H<sub>2</sub>TPP(DDQ)<sub>2</sub> in acetonitrile facilitated the use of acetonitrile as a safer solvent than the common chlorinated solvents in photooxidation reactions. Also, the influence of different parameters including the type and power of light source, type of solvent and the molar ratio of H<sub>2</sub>TPP(DDQ)<sub>2</sub> to olefin on the efficiency of the catalyst and the quantum yield of the photochemical reaction ( $\Phi$ ) was investigated. The use of 1,3-diphenylisobenzofuran as the quencher of singlet oxygen and 1,4-benzoquinone as the scavenger of superoxide radical anion revealed the involvement of singlet oxygen as the major ROS species.

## Introduction

In view of the fact that the activated forms of molecular oxygen such as singlet oxygen, superoxide anion and hydrogen peroxide, have versatile and advantageous applications<sup>1-6</sup>, in photodynamic cancer therapy (PDT), fine chemical synthesis and wastewater treatment, different strategies have been utilized to activate  $O_2$  as the most abundant and green terminal oxidant<sup>7-13</sup>. In this regard, photoactivation of  $O_2$  catalyzed by porphyrins, phthalocyanines, and related tetrapyrroles was extensively used to produce the activated species of molecular oxygen<sup>14-20</sup>. Aerobic photocatalytic oxidation of organic substrates catalyzed by porphyrin and metalloporphyrin sensitizers has been extensively studied and well documented during the past decades<sup>21-28</sup>. However, as an unwanted parallel reaction, partial or complete decomposition of some porphyrin-based photosensitizers has been observed

under oxidative conditions<sup>29</sup> and therefore the increased stability of the sensitizer should be considered in designing new porphyrinic photosensitizers<sup>30,31</sup>. The introduction of electron-withdrawing and sterically demanding substituents at the porphyrin periphery are the main approaches commonly employed to overcome the problem<sup>21,32-35</sup>. On the other hand, core substitution may be used as an alternative method to increase electron-deficiency on the porphyrin macrocycle; the formation of 1:2 donor-acceptor complexes between porphyrins and different  $\sigma$  and  $\pi$ -acceptors is accompanied with the shift of electron density from the central pyrrolenine nitrogen atoms to the acceptor molecules<sup>36-42</sup>. Also, the presence of two acceptor molecules above and below the porphyrin mean plane increases the steric hindrance around the porphyrin molecule<sup>37,39,40,43</sup> that probably enhances the stability of porphyrin towards oxidative attack by different oxidants. In other words, the steric and electronic effects caused by the core substitution of porphyrin are expected to increase the photostability of the aromatic macrocycle. Furthermore, the molecular complexation of porphyrins with Lewis acids was found to be associated with the red shift of absorption maxima (the Soret band) of porphyrins<sup>44,45</sup>. From the application point of view, the ability of photosensitizers to absorb longer wavelength seems to be useful in the treatment

<sup>&</sup>lt;sup>a.</sup>Address here.

<sup>&</sup>lt;sup>b.</sup>Address here.

<sup>&</sup>lt;sup>c.</sup> Address here.

<sup>&</sup>lt;sup>†</sup> Footnotes relating to the title and/or authors should appear here.

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of highly pigmented tumors in PDT<sup>46</sup>; it should be noted that the maximum penetration power into most human tissues is in the 650-850 nm spectral region known as phototherapeutic window<sup>47</sup>.To our knowledge, to date there has been no report on the photocatalytic activity of porphyrin molecular complexes in the aerobic oxidation of organic compounds. In the present work, the photocatalytic performance and oxidative stability of meso-tetraphenylporphyrin and its 2,3dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, Figure 1) adduct in the aerobic oxidation of cyclooctene and cyclohexene have been studied. Moreover, molecular complexation of mesotetraphenylporphyrin (H<sub>2</sub>TPP, Figure 1) with DDQ was found to substantially increase its solubility in acetonitrile as a nonchlorinated solvent that facilitated the use of acetonitrile as a safer solvent than the common chlorinated solvents in photooxidation reactions. It is noteworthy that to date there is no x-ray crystallographic structure available to the 1:2 molecular complexes of meso-tetraphenylporphyrins and DDQ. However, Mohajer et al.<sup>48</sup> suggested a saddle shaped conformation (Figure 1) for the molecular complex on the basis of the similarities observed between the  $^1\mathrm{H},\,^{13}\mathrm{C}\,\mathrm{NMR}$  and UV-vis spectra of the molecular complexes and the corresponding dications.



Figure 1. H<sub>2</sub>TPP, DDQ and the proposed structure of H<sub>2</sub>TPP(DDQ)<sub>2</sub><sup>48</sup>.

## **Experimental section**

## Instrumental

The NMR spectra were obtained in  $CDCl_3$  on a Bruker Avance DPX-400 MHz spectrometer. The absorption spectra were recorded on a Pharmacia Biotech Ultrospec 4000 UV–Vis spectrophotometer. A Varian-3800 gas chromatograph equipped with a HP-5 capillary column (phenylmethyl siloxane

 $30 \text{ m} \times 320 \text{ }\mu\text{m} \times 0.25 \text{ }\mu\text{m}$ ) and a flame-ionization detector was utilized in GC alalyses.

## Preparation of H<sub>2</sub>TPP and H<sub>2</sub>TPP(DDQ)<sub>2</sub>

H<sub>2</sub>TPP was synthesized and purified according to the literature methods<sup>49</sup> The spectral data are summarized in the in the ESI,<sup>†</sup> S1. H<sub>2</sub>TPP(DDQ)<sub>2</sub> was prepared using the procedure reported by Mohajer et al.<sup>48</sup>; H<sub>2</sub>TPP and DDQ were added to CH<sub>2</sub>Cl<sub>2</sub> in 1:2 molar ratio. The solution was stirred at room temperature for 3-4 days. The progress of the reaction was monitored by UV-vis spectroscopy; the disappearance of the band at ca. 417 nm due to the free base porphyrin showed the completeness of reaction. Slow evaporation of CH<sub>2</sub>Cl<sub>2</sub> at room temperature gave a dark green solid that was characterized by UV-vis, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (ESI,<sup>+</sup>S2).

## General oxidation procedure

The photooxidation reactions were carried out in a double walled cylindrical glass vessel equipped with water circulation through the wall to maintain a constant temperature (ESI,+ S3). In a typical reaction, the photosensitizer  $(6.6 \times 10^{-4} \text{ mmol})$ and olefin (0.66 mmol) were added in 1:1000 molar ratio to the respective solvent. In the case of perfluorodecalin/toluene and perfluorodecalin/DCE emulsions as the reaction media, the photosensitizer and olefin dissolved in toluene or 1,2dichloroethane (DCE) were added to perfluoro solvent and the reaction mixture was stirred vigorously under biphase conditions. At the end of the reaction, perfluorodecalin was separated by a separatory funnel and the other phase was analyzed as follows. In all photooxidation reactions oxygen at 1 atm pressure was bubbled through the stirred solution upon irradiation for the required time. The resulting solution was directly analyzed by <sup>1</sup>H, <sup>13</sup>C NMR and gas chromatography. Also, the KI test<sup>50</sup> was used to confirm the formation of allylic hydroperoxide. The oxidation of cyclooctene and cyclohexene gave Cyclooct-1-en-3-yl hvdroperoxide and 2-cyclohexene-1one as the sole product, respectively. The spectral data of the products are summarized in the in the ESI.<sup>+</sup> S4 and S5.

## **Chemical actinometry**

According to the literature<sup>51-55</sup>, the most reliable method to determine the effective light intensity is based on chemical actinometry. In order to calculate the rate of photon absorption known as the photon flux for our photoreaction system upon exposure to blue LED lamps, we utilized a potassium ferrioxalate actinometer with known quantum yield up to 550 nm<sup>55</sup> (see ESI,<sup>†</sup> S7 for details of actinometery).

## **Results and Discussion**

## Photooxidation of cyclooctene

Aerobic photooxidation of cyclooctene in the presence of the DDQ molecular complex of  $H_2$ TPP led to the formation of the corresponding allylic hydroperoxide as the sole product. Due to the influence of parameters such as the molar ratio of catalyst:substrate, solvent, and the nature of photosensitizer

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on the efficiency of the oxidation reactions, the optimum reaction conditions were determined; different molar ratios of catalyst:olefin were examined (Table 1) and the 1:1000 molar ratio was found to be the optimum one. It is observed that the catalyst:olefin molar ratio has little effect on the catalyst stability. However, the maximum turnover number (TON) was achieved at the 1:1000 molar ratio. It should be noted that TON which shows the number of moles of product obtained per one mole of the catalyst is used as a criterion of the catalyst efficiency<sup>56</sup>.

 Table 1. The optimization of the reaction conditions for different molar ratios of

  $H_2$ TPP(DDQ)<sub>2</sub>:cyclooctene (1:X) upon irradiation with a 150 W metal halide lamp<sup>a</sup>.

Entry	Catalyst:cyclooctene (1:X)	Conversion (%)	Oxidative stability (%) <sup>b</sup>	TON
1	1:100	84	98	84
2	1:500	84	96	420
3	1:700	71	90	497
4	1:1000	80	95	800
5	1:2000	30	92	600

 $^a$  The photooxygenation reactions were performed using 6.6  $\times$  10<sup>-4</sup> mmol of the catalyst in CCl<sub>4</sub> for 72 h.  $^b$  The oxidative stability of  $\,H_2 TPP(DDQ)_2$  was determined by UV-vis spectrum of the reaction mixture at a given time.

Furthermore, various types of light source including 10 and 20 W red and blue high power LED lamps (Table 2) and a 150 W metal halide lamp (Tables 3-6) were used as the light source. In all the solvents, the blue lamp is much better than the red lamp of the same power on the basis of the obtained quantum efficiency of the oxidation reaction ( $\Phi$ ), conversion, TON and turnover frequency (TOF) values. Also, the use of a 20 W LED lamp led to a significant increase in the efficiency of the reaction in the used solvents.

The absorption spectrum of H<sub>2</sub>TPP(DDQ)<sub>2</sub> and the emission spectrum of the blue and red LED lamps are shown in Figure 2. It is observed that the Soret and Q(0,0) bands of the adduct overlap with the emission bands of the blue (440-520 nm) and red (600-700 nm) LED lamps, respectively. Much higher efficiency of the blue LED lamps than the red ones seems to be due to the higher absorption intensity of the adduct in the Soret band region.

by LED lamps for 72 h.						
Entry	LED lamp	Solvent	Conversion [stability] <sup>a</sup> (%)	$\Phi^{b}$	TON (TOF) <sup>c</sup> (h <sup>-1</sup> )	
1	Blue (10 W)	DCE	45 [87]	0.16	450 (6.3)	
2	Blue (10 W)	Toluene	30 [89]	0.11	300 (4.2)	
3 <sup>d</sup>	Blue (10 W)	Toluene	18 [74]	0.06	180 (2.5)	
4	Blue (20 W)	DCE	90 [15]	0.62	900 (14.5)	
5 <sup>d,e</sup>	Blue (20 W)	DCE	43 [0]	0.25	430 (5.9)	
6	Blue (20 W)	Toluene	33 [98]	0.2	330 (4.6)	
7	Blue (20 W)	CH₃CN <sup>f,g</sup>	-	-	-	
8	Red (10 W)	DCE	10 [69]	0.03	100 (1.4)	
9	Red (10 W)	Toluene	Trace	-	-	
10	Red (20 W)	DCE	29 [91]	0.04	290 (4.0)	
11	Red (20 W)	Toluene	Trace	-	-	

Table 2. The oxidation of cyclooctene in the presence of H<sub>2</sub>TPP(DDQ)<sub>2</sub> (1:2) irradiated

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<sup>a</sup> The data in the bracket is the oxidative stability of the photosensitizer (%). <sup>b</sup> The quantum efficiency of the reaction is defined as the number of the reacted molecules divided by the number of photons absorbed per time unit<sup>55</sup>: For more details see the experimental section. <sup>c</sup> TOF was obtained as turnover number of the reaction per time unit. <sup>d</sup> The oxidation reaction was carried out in the presence of H<sub>2</sub>TPP. <sup>e</sup> The reaction was carried out under basic condition of tetra-n-butylammonium hydroxide (0.5 ml). <sup>f</sup> The reaction was conducted at -10 <sup>c</sup>C. <sup>g</sup> The adduct was partially dissociated to H<sub>2</sub>TPP and DDQ and therefore the reaction was terminated.



Figure 2. The absorption spectrum of H\_2TPP and H\_2TPP(DDQ)\_2 in CH\_2Cl\_2; the insets a and b show the emission spectrum of the blue and red LED lamps.

The reaction was also performed in acetonitrile (Table 2, entry 7). Due to the presence of an equilibrium between  $H_2TPP(DDQ)_2$ ,  $H_2TPP$  and DDQ in acetonitrile and partial dissociation of the molecular complex into its constituents ( $H_2TPP$  and DDQ) at room temperature, the reaction was conducted at -10 °C. However, the exposure of the reaction mixture to the 20 W blue LED lamp again led to the same observation and therefore the reaction was performed using a 150 W metal halide lamp (Table 3).

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Table	3.	The	oxidation	of	cyclooctene	in	the	presence	of	$H_2TPP$	and
H <sub>2</sub> TPP(	DD	Q)2 (1	:2) irradiat	ed	by a 150 W m	etal	halio	de lamp in	acet	tonitrile	

Entry	Photosensitizer	Conversion (%)	Time (h)	TON (TOF) (h <sup>-1</sup> )
1	DDQ <sup>a</sup>	Trace	72	-
2	H₂TPP <sup>a,b</sup>	32	72	320 (4.4)
3	H₂TPP <sup>b,c</sup>	55	72	550 (7.6)
4	H₂TPP(DDQ)₂ (1:2) <sup>d</sup>	69	34 <sup>e</sup>	690 (20.3)
5	H <sub>2</sub> TPP(DDQ) <sub>2</sub> (1:2) <sup>a</sup>	65	48 <sup>e</sup>	650 (14.4)

<sup>a</sup> The reaction was performed at -10 °C. <sup>b</sup> H<sub>2</sub>TPP ( $6.6 \times 10^{-4}$  mmol) dissolved in 10 µl dichloromethane was added to 10 ml acetonitrile as the reaction media. <sup>c</sup> Room temperature. <sup>d</sup> The reaction temperature was (0-5) °C. <sup>e</sup> The reaction was continued up to a point of partially or completely dissociation of the adduct into its constituents.

Herein,  $H_2TPP(DDQ)_2$  was stable up to 48 h at -10 °C and a conversion of 65% was obtained (entry 5). Also, the catalytic activity of the free base porphyrin and the adduct was compared (entries 2 and 5). The results show an increase of 33 % in the conversion for the reaction catalyzed by the latter accompanied by a decrease in the reaction time from 72 to 48 h.

The oxidation reaction was also conducted in the presence of  $H_2TPP(DDQ)_2$  irradiated by a 150 W metal halide lamp in the chlorinated solvents (Table 4). However, the use of a 20 W LED lamp (Table 2, entry 4) instead of the metal halide lamp (Table 4, entry 4) gave much higher conversion of cyclooctene in DCE. It should be noted that no detectable difference was observed between the oxidative stability of the adduct in the presence of the LED and metal halide lamps (Figure 3).

The increase of temperature is usually accompanied with an increase in the reaction rate<sup>57</sup>. The comparison of the data obtained in the presence of  $H_2$ TPP (Table 3, entries 2 and 3) and  $H_2$ TPP(DDQ)<sub>2</sub> (entries 4 and 5) confirms the point. However, in the case of the latter, the increase of reaction temperature was associated with higher degrees of dissociation of the adduct (vide supra).

The oxidation of cyclooctene was also carried out by filtering the emission spectrum of the metal halide lamp below and above the 436 nm band of the lamp (Table 4, entry 5). It is noteworthy that the Soret band of  $H_2TPP(DDQ)_2$  appears around 440 nm and therefore the choice of this emission band allows us to evaluate the main absorption region involved in the photocatalytic activity of the adduct. The comparison of the entries 4 and 5 shows that the conducting of reaction in this condition led to a conversion comparable with that observed in the absence of the filters. The results are in accord with the significantly enhanced efficiency of the blue LED lamps relative to the red ones (Table 2, entries 4, 10 and entries 1, 8).  $\label{eq:table_transform} \begin{array}{l} \textbf{Table 4.} \ \mbox{The oxidation of cyclooctene in the presence of $H_2$TPP and $H_2$TPP(DDQ)_2$} \\ (1:2) \ \mbox{irradiated by a 150 W metal halide lamp in chlorinated solvents for 72 h.} \end{array}$ 

Entry	Catalyst	Solvent	Conversion	Oxidative	TON
			(%)	stability (%)	
1	DDQ	CCl <sub>4</sub> (or	Trace	0	-
		DCE)			
2	H₂TPP <sup>a</sup>	$CCI_4$	33	10	330
3	$H_2 TPP^a$	DCE	78 <sup>b</sup>	12 <sup>c</sup>	780
4	H <sub>2</sub> TPP(DDQ) <sub>2</sub>	DCE	40	91	400
	(1:2)				
5	H <sub>2</sub> TPP(DDQ) <sub>2</sub>	DCE	32 (0.64) <sup>c,d</sup>	87	320
	(1:2)				
6	$H_2TPP(DDQ)_2$	$CCI_4$	61 (1 <sup>st</sup> run) <sup>c</sup>	81 <sup>°</sup>	610
	(1:2)		82 (2 <sup>nd</sup> run) <sup>c</sup>	5 <sup>e</sup>	1140
7	$H_2TPP(DDQ)_2$	DCE	85	59	850
	(1:6)				

<sup>a</sup> The reaction was carried out under basic condition of tetra-n-butylammonium hydroxide (0.5 ml). <sup>b</sup> 48 h. <sup>c</sup> 72 h. <sup>d</sup> The reaction has been done in the presence of liquid filter solutions. The data in parenthesis is the quantum yield ( $\Phi$ ) of the reaction at 436 nm: For more information see chemical actinometry in the experimental section. <sup>e</sup> 144 h.



Figure 3. The oxidative stability of  $H_2$ TPP, 1 and  $H_2$ TPP(DDQ)<sub>2</sub>, 2 in oxidation reactions of cyclooctene performed in 1,2-dichloroethane and toluene upon irradiation by LED and metal halide lamps for 72 h.

The nature of the solvent was found to play a crucial role in the efficiency of the aerobic photooxidation reactions due to molecular oxygen solubility and the lifetime of singlet oxygen. According to the literature, different chlorinated<sup>21,29,30,31,32,58-</sup> <sup>60</sup>. non-chlorinated<sup>26,61-64</sup> solvents and perfluorocarbons<sup>29,65-70</sup> have been used in these studies. The oxidation of cyclooctene was conducted in CCl<sub>4</sub>, 1,2-dichloroethane (DCE), acetonitrile, toluene, CDCl<sub>3</sub> and the emulsions of perfluorodecalin (PFD) in combination with DCE or toluene (Table 5). In this regard, perfluorinated solvents were found to increase both the solubility of molecular oxygen and the lifetime of singlet oxygen<sup>63</sup>. According to Table 5, higher conversions and TON were achieved in CDCl<sub>3</sub> and perfluorodecalin/dichloroethane. This observation provides evidence of the involvement of singlet oxygen as the major reactive oxygen species in this reaction. Also, the concentration of the photosensitizer was increased in case of the latter (entries 8 and 9); a five-fold increase in the concetration of the catalyst led to small increases (5-20%) in the conversion.

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Table 5. Solvent effects on the oxidation reactions of cyclooctene catalyzed
by $H_2TPP(DDQ)_2 (1:2)^{a}$

Entry	Solvent	Conversion (%)	TON (TOF) (h <sup>-1</sup> )
1	Toluene	26	260 (3.6)
2 <sup>b</sup>	Toluene	75	750 (10.4)
2	CDCl <sub>3</sub>	87	870 (12.1)
3	CCl <sub>4</sub>	64	640 (8.9)
4	DCE	40	400 (5.6)
5	Solvent free	4 <sup>c</sup>	400 (8.0)
6	PFD + DCE <sup>d</sup>	87	870 (12.1)
7	PFD + Toluene <sup>d</sup>	36	360 (5.0)
8	PFD + DCE	92 <sup>e</sup>	920 (12.8)
9	PFD + Toluene	56 <sup>e</sup>	560 (7.8)

<sup>a</sup> The reaction mixture was irradiated by a 150 W metal halide lamp for 72 h. <sup>b</sup> The oxidation reaction was catalysed by H<sub>2</sub>TPP ( $6.6 \times 10^{-4}$  mmol). <sup>c</sup> The reaction was performed in 1:10000 molar ratios of catalyst:cyclooctene for 50 h. <sup>d</sup> The emulsion solutions of PFD in combination with dichloroethane or toluene were used as the solvent. <sup>e</sup> A 5-fold increase in the catalyst concentration was used in the reaction.

the case of DCE, the use of adduct as catalyst was accompanied with significant increase in the oxidative stability of the catalyst.

**Table 6.** The oxidation of cyclohexene in the presence of  $H_2TPP$  and  $H_2TPP(DDQ)_2$  (1:2) irradiated by a 150 W metal halide lamp in chlorinated solvents for 72 h.

Entry	Catalyst	Solvent	Conversion (%)	Oxidative stability (%)	TON (TOF) (h <sup>-1</sup> )
1	DDQ	CCl <sub>4</sub> (or DCE)	Trace	0	-
2	H <sub>2</sub> TPP <sup>a</sup>	CCI <sub>4</sub>	17	26	170 (2.4)
3	H₂TPP <sup>a</sup>	DCE	70	59	700 (9.7)
4	H <sub>2</sub> TPP(DDQ) <sub>2</sub> (1:2)	CCI <sub>4</sub>	55	57	550 (7.6)
5	H <sub>2</sub> TPP(DDQ) <sub>2</sub> (1:2)	DCE	22	96	220 (3.1)
6	H₂TPP(DDQ₂ (1:6)	DCE	32	97	320 (4.4)

<sup>a</sup> The reaction was carried out under basic condition of tetra-n-butylammonium hydroxide (0.5 ml).

## H<sub>2</sub>TPP(DDQ)<sub>2</sub> versus H<sub>2</sub>TPP

In order to summarize the results obtained in the oxidation of cyclooctene under different conditions, the time courses of the formation of oxidation product of cyclooctene are shown in Figure 4. It is observed that within a time course of 72 h, the maximum yield was achieved in the presence of  $H_2TPP(DDQ)_2$  and a 20 W blue LED lamp in DCE.



Figure 4. Time course of the formation of Cyclooct-1-en-3-yl hydroperoxide obtained in the photooxidation of cyclooctene in the presence of  $H_2TPP(DDQ)_2$ .

## Photooxidation of cyclohexene

The oxidation of cyclohexene in the presence of  $H_2TPP(DDQ)_2$ in CCl<sub>4</sub> and DCE (Table 6) gave 2-cyclohexen-1-one as the sole product. In CCl<sub>4</sub> remarkable increases in the catalyst oxidative stability and conversion were observed for the reaction catalyzed by the adduct in comparison with that performed in the presence of the free base porphyrin (entries 2 and 4). In

The formation of molecular complex between H<sub>2</sub>TPP and DDQ was expected to increase the oxidative stability of the porphyrin center. Also, the red shift of the absorption bands resulted in by the adduct formation was expected to increase the overlap between the absorption bands of porphyrin and the emission bands of the light source. The photocatalytic activity of H<sub>2</sub>TPP and H<sub>2</sub>TPP(DDQ)<sub>2</sub> was compared in the presence of the best light source i.e. the 10 and 20 W blue LED lamps (Table 2, entries 2 and 3, also entries 4 and 5). The results show significant increase in the conversion of the reaction performed in the presence of the adduct compared to that catalyzed by the free base porphyrin. Also, the oxidative stability of the adduct was greater than the free base porphyrin. In the case of the 150 W metal halide lamp (Table 4, entries 2 and 6), the increase in the oxidative stability and the conversion were much more than those observed in the presence of the LED lamps.

## The effect of excess DDQ

The presence of excess amounts of DDQ shifts the equilibrium between the free base porphyrin and the adduct toward  $H_2TPP(DDQ)_2$ . Accordingly, the effect of excess DDQ on the photocatalytic activity of  $H_2TPP(DDQ)_2$  was studied (Table 4, entries 4, 7 and also Table 6, entries 5, 6) and an increase in the conversion of cyclohexene and cyclooctene to the oxidation products was observed in DCE.

## The formation of porphyrin dication

In spite of the fact that porphyrin free bases may form diprotonated species upon exposure to the UV-vis light in chlorinated solvents<sup>32,71</sup>, these solvents have been extensively used in porphyrin catalyzed photooxidation of organic

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compounds<sup>21,29,30-32,58-60</sup>. However, in some studies, the decreased catalytic efficiency of the porphyrin free bases was attributed to the formation of porphyrin diacids<sup>31</sup>. Interestingly, UV-vis spectra of H<sub>2</sub>TPP(DDQ)<sub>2</sub> showed that the adduct was completely stable under the acidic condition formed by the formation of acid in DCE and  $CCl_4$  (Figure 5). This stability is probably due to the coordination of the pyrrolenine nitrogen atoms to the DDQ molecules. In other words, the formation of donor-acceptor molecular complex between H<sub>2</sub>TPP and DDQ significantly decreases the basicity of porphyrin molecule. As is observed in Figure 5, the Q(0,0) band of the porphyrin diacid that was prepared by the addition of acidic DCE to H<sub>2</sub>TPP appears at 662 nm. On the other hand, the Q(0,0) band due to the adduct appears at 655 nm. It should be noted that the UV-vis spectrum of the diacid and H<sub>2</sub>TPP(DDQ)<sub>2</sub> were prepared using a solution with the same concentration as that was used in the oxidation reactions. In this concentration, the Soret band are observed as a very intense broad band and therefore the wavelength of the Q(0,0) band was used in this comparison. Furthermore, the gradual addition of acidified  $CDCl_3$  to the solution of  $H_2TPP(DDQ)_2$  in pure  $CDCl_3$  (with no acid impurity) led to no detectable change in the position of the resonance of different protons. The NH signal of the adduct at  $\delta$  -0.36 ppm is significantly upfield shifted with respect to that of the H<sub>2</sub>TPP dication ( $\delta$  0.35 ppm)<sup>48</sup>. The <sup>1</sup>H NMR spectrum of the adduct in the NH region in the presence of different amounts of acidic CDCl<sub>3</sub> was shown in the ESI,<sup>+</sup> S6.



**Figure 5.** a) The absorption spectra of H<sub>2</sub>TPP (purple curve), (DDQ)<sub>2</sub>H<sub>2</sub>TPP (2:1) (solid green curve), H<sub>2</sub>TPP solution in DCE irradiated by a 150 W metal halide lamp for 19 h in the absence of any base (dotted green curve) and H<sub>2</sub>TPP(HCl)<sub>2</sub> (dashed green curve). b) The Q(0,0) band of H<sub>2</sub>TPP, (DDQ)<sub>2</sub>H<sub>2</sub>TPP (2:1), H<sub>2</sub>TPP dication (in DCE acidified by light exposure) and H<sub>2</sub>TPP(HCl)<sub>2</sub> (prepared by HCl treatment of H<sub>2</sub>TPP<sup>72</sup>) appears at 645, 655, 662, 662 nm, respectively.

On the other hand, the oxidation of cyclooctene was conducted in the presence of protonated  $H_2$ TPP in DCE; the solution containing  $H_2$ TPP and cyclooctene in 1:1000 molar ratio was irridiated with a 150 W metal halide lamp in the absence of any alkaline additive such as NaHCO<sub>3</sub> that has been previously utilized to neutralize the protonated porphyrin in photooxidation experiments<sup>32</sup>. The UV-vis spectrum of the reaction mixture after ca. 6 h showed complete disapperance of the Q(0,0) band at 645 nm that revealed the absence of free base  $H_2$ TPP. The aerobic photooxidation of cyclooctene in this condition led to the complete degradation of the porphyrin

diacid within 24 h. It should be noted that under the same reaction condition with  $H_2TPP(DDQ)_2$  as the catalyst, the adduct was stable after 72 h (Table 4, entry 4).

## Proposed mechanism

According to the literature, singlet oxygen and superoxide radical anion species are involved in the photooxidation reactions catalyzed by nonmetalated porphyrins.<sup>4,26,28,73,74</sup> To prove the mechanism of the oxidation reaction, we firstly used an oxygen singlet quencher (scavenger). Chemical reaction between singlet oxygen and 1,3-diphenylisobenzofuran (DPBF) was monitored by following the emission spectrum of DPBF. A significant decrease was observed in the intensity of the emission band at 480 nm that was in accord with the presence of oxygen singlet (Figure 6). In another test, 1,4-benzoquinone as the quencher of superoxide radical anion was added to the reaction mixture. The oxidation of cyclooctene was conducted in the presence of  $H_2TPP(DDQ)_2$  using a 20 W blue LED lamp as the light source in DCE. The conversion of reaction was nearly the same (ca. 30%, for a reaction time of 10 h) in the presence and the absence of 1,4-benzoquinone that confirms the absence of superoxide species in the catalytic cycle of the reaction.



Figure 6. The spectral changes in the emission spectrum of 1,3-diphenylisobenzofuran under the reaction conditions.

According to the above discussion, a mechanism was proposed (Scheme 1).



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## Conclusion

In this study, the 1:2 adduct of  $H_2TPP$  with DDQ has been used for the first time as photosensitizer in the aerobic photooxidation of cyclooctene and cyclohexene in DCE,  $CCl_4$ , acetonitrile, toluene,  $CDCl_3$ . The oxidation reactions were also conducted under fluorous biphase system (FBS) using perfluorodecalin/DCE and perfluorodecalin/toluene mixtures. Also, LED and metal halide lamps were used as the light source. It was found that:

- i. The adduct showed a remarkably increased catalytic efficiency and oxidative stability compared to that of the free base porphyrin, under the optimized reaction conditions.
- ii. The photosensitizing ability of the adduct was found to be essentially determined by the light absorption in the Soret band region that is in accord with the much higher efficiency of the blue LED lamps than that of the red ones.
- iii. The protonation of  $H_2$ TPP was found to be efficiently prevented by complexation to the DDQ molecules.
- iv. The out-of-plane deformation of porphyrin core and the increased polarity of the aromatic macrocycle caused by the adduct formation between H<sub>2</sub>TPP and DDQ led to a significant increase in its solubility in acetonitrile. This in turn facilitated the use of acetonitrile as a safer solvent in photooxidation reactions catalyzed by porphyrin-based photosensitizers.
- v. The remarkable quencing of the flouresence of 1,3diphenylisobenzofuran and little effect of 1,4benzoquinone on the conversion of cyclooctene to the oxidation product showed the formation of singlet oxygen as the main photogenerated active species under reaction conditins.

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# A novel porphyrinic photosensitizer based on the molecular complex of meso-tetraphenylporphyrin with 2,3-dichloro-5,6-dicyano-1,4benzoquinone: Higher photocatalytic activity, photooxidative stability and solubility in non-chlorinated solvents

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The 1:2 molecular complex of meso-tetraphenylporphyrin with 2,3-dichloro-5,6dicyanobenzoquinone (DDQ) has been used as a promising photosensitizer for the aerobic oxidation of olefins in different chlorinated and non-chlorinated solvents.

