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Effects of β -bromine substitution and core protonation on photosensitizing properties of porphyrins: Long wavelength photosensitizers

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ABSTRACT

In this study, a series of β -brominated meso-tetraphenylporphyrins, H₂TPPBr_x (x = 2, 4, 6 and 8) with remarkably red shifted absorption bands towards the longer wavelengths of the visible light known as therapeutic window and their diprotonated analogues were used as photosensitizers in the aerobic oxidation of cyclooctene to investigate the influence of degree of β bromination on the photocatalytic activity and oxidative stability of H₂TPP. Furthermore, the β brominated porphyrins showed significantly decreased fluorescence quantum yields (φ_F) and radiative decay rate constants but increased nonradiative decay rate constants. The highest catalytic activity was observed in the case of the partially brominated porphyrins, H₂TPPBr₂ and H₂TPPBr₄. While, H₂TPPBr₂ and H₂TPPBr₄ were as stable as H_2 TPP, the oxidative degradation of H_2 TPPBr₆ and H_2 TPPBr₈ was remarkably higher than that of the non-brominated porphyrin. A good correlation was observed between the photocatalytic activity of H₂TPPBr_x and their diprotonated species and the singlet oxygen quantum yields (ϕ_{Δ} = 0.02–0.21 and 0.12 to 0.59, respectively), determined chemically through the reaction of singlet oxygen with 1,3diphenylisobenzofuran (DPBF). In order to examine the effects of steric hindrance on the photocatalytic properties of the brominated porphyrins, β tetra-brominated derivative of meso-tetra(2-methylphenyl) porphyrin, H₂T(2-Me)PPBr₄ with bulky methyl substituents at the ortho positions was prepared and compared with H₂TPPBr₄. The steric hindrance caused by the presence of four methyl groups could improve the oxidative stability of the photosensitizer by 30 to 50% at the cost of significant loss of photocatalytic activity. On the other hand, diprotonation of H₂TPPBr_x with weak and strong acids (CH₂ClCOOH and CF₃COOH) was found to be an efficient approach to overcome the extensive oxidative degradation of these photosensitizers, with concomitant red shift of the absorption bands to 451-490 and 674-743 nm, in the Soret and Q band regions, respectively.

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1. Introduction

Porphyrins, porphyrinoids and their derivatives are among the most efficient photosensitizers have been used in different applications such as environmental control, wastewater treatment, photo-dynamic therapy, medicine and photocatalysis of organic transformations [1–9]. In this regard, porphyrin derivatives with red shifted absorption bands are of great interest from an application point of view [1,10,11]. The introduction of bromine atoms at the porphyrins periphery is accompanied with the red shift of the Soret and Q bands [12,13]. Accordingly, β brominated porphyrins may be used as red shifted counterparts of simple porphyrins such

as *meso*-tetraphenylporphyrin (H₂TPP). On the other hand, the use of porphyrins and porphyrinoids as photosensitizers in different applications is associated with extensive oxidative degradation of the aromatic macrocycle and therefore many attempts were made to design photosensitizers with increased oxidative stability under reaction conditions [14–15]. The later may be achieved by introduction of electronegative and/or bulky atoms at the meso and β positions [16–19]. Furthermore, the presence of bromine atoms at the porphyrins periphery influences the optical properties of porphyrins [12,13]; due to the heavy atom effect, the fluorescence quantum yield of β -brominated porphyrins. This in turn facilitates the S₁ to T₁ intersystem crossing which is necessary for the photosensitized production of singlet oxygen from triplet molecular oxygen [15]. The substitution of β positions with bromine atoms also

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leads to the structural changes in the porphyrins core that is usually the out-of-plane deformation of the aromatic macrocycle to a saddled or ruffled one[12,13].

The presence of heavy atoms at the porphyrin periphery which is favor of the S₁ to T₁ intersystem crossing process [15], electronwithdrawing effects of the bromine atoms, the red shifted absorption bands and remarkably decreased fluorescence quantum yield of β brominated porphyrins [13] make them potential candidates for developing new photosensitizers. However, no attention was paid to the influence of β bromination on the photosensitizing efficacy of meso-tetra(aryl)porphyrins. In continuing our studies on the photocatalytic performance of porphyrin derivatives, a series of β brominated porphyrins with 2 to 8 bromine atoms at the pyrrole ring, H₂TPPBr_x (Fig. 1) were used as photosensitizers in the aerobic photooxidation of olefins in various mixed solvents consisting of water, acetonitrile and toluene. The main objective of this work is to study the influence of degree of bromination on the photocatalytic activity and oxidative stability of H₂TPP. We have recently reported the optical properties of β brominated H₂TPP with 2 to 8 bromine atoms in a comparative study [13]. The absorption bands of the novel photosensitizers were found to shift towards the phototherapeutic window in the range of 600 and 800 nm. The latter makes them potential candidates for applications such as photodynamic therapy [1].

2. Experimental

2.1. Instrumental and reagents

An Ultraspec 3100 Pro spectrophotometer was used for recording UV-Vis absorption spectra. Fluorescence spectra and quantum yields were obtained from dichloromethane solutions of the porphyrins in a high precision quartz fluorescence cell on a Cary Eclipse fluorescence spectrophotometer. ¹H NMR spectra were recorded in CDCl₃ on a BrukerAvance DPX-400 MHz spectrometer. The reaction mixtures were analyzed using a Varian-3800 gas chromatograph with a HP-5 capillary column and flameionization detector. In order to characterize the oxidation products, control reactions were conducted in CDCl₃ under the same conditions. The ¹³C NMR spectrum of the reaction mixture prepared after the required time confirmed the formation of cyclooct-1en-3-yl hydroperoxide and 2-cyclohexene-1-one in the oxidation of cyclooctene and cyclohexene, respectively (See supplementary material). More details of the experimental setup were explained in our previous [14]0.10 W blue, white and red LED lamps were as the light source (8 mm diameter with full width at half maximum less than ca. 20 nm for the most intense emission bands, see supplementary material for the full emission spectra). Benzaldehyde and 2-methylbenzaldehyde (for synthesis, Merck) were used as received. Pyrrole (Fluka, for synthesis) was distilled before use. Trifluroacetic acid (ReagentPluss 99%,), chloroacetic acid (for synthesis, Sigma-Aldrich) and propionic acid (Merck) were used as received. N-bromosuccinamide (NBS) was recrystallized from hot water and dried at 80 °C under vacuum. Dichloromethane which was used for the synthesis of the dications was dried over anhydrous calcium chloride and distilled over CaH₂. Cyclooctene and cyclohexene (Sigma-Aldrich) were passed through a silicagel column before use and their purity was confirmed by NMR spectroscopy.1,3-diphenylisobenzofuran (97%, Sigma-Aldrich) and1,4-benzoquinone (reagent grade, >98%, Sigma-Aldrich) were used as received.

2.2. Chemical determination of singlet oxygen quantum yields

The Φ_{Δ} value of H₂TPPBr_x was measured through the reaction of singlet oxygen with 1,3-diphenylisobenzofuran (DPBF) as a specific singlet oxygen quencher and H₂TPP ($\Phi_{\Delta} = 0.70$ in acetonitrile) [20] as a reference photosensitizer, using the equation $\Phi_{\Delta} = \Phi_{\Delta}^{std} \times (\upsilon_i \times I^{std}/\upsilon_i^{std} \times I)$ proposed by Murata et al.[21]. In this equation, Φ_{Δ} , Φ_{Δ}^{std} , υ_i , I^{std} , υ_i^{std} and I present the Φ_{Δ} of H₂TPPBr_x, the rate of DPBF (8 × 10⁻⁴ M) oxidation in the presence of the respective brominated porphyrin and a 10 W red LED lamp, the rate of DPBF oxidation in the presence of methylene blue, the number of photons absorbed by the standard solution and those absorbed by the photosensitizer, respectively (More details were described elsewhere) [14,18,19,22]. All measurements were conducted in



Fig. 1. Aerobic photooxidation of cyclohexene and cyclooctene to 2-cyclohexene-1-one and cyclooct-1-en-3-yl hydroperoxide catalyzed by porphyrins and β-brominated porphyrins.

time intervals less than 800 s, where no catalyst degradation was observed for the brominated porphyrins.

2.3. Fluorescence quantum yield (Φ_f)

The fluorescence spectra were obtained using dilute solution $(\sim 10 \ \mu\text{M})$ of porphyrins in dichloromethane, purged with N₂ gas to remove oxygen [13]. The porphyrin solutions were excited at the Soret band of the respective porphyrin and the emission spectra were recorded in the range of 500 to 800 nm. Also, the fluorescence quantum yields were calculated relative to that of H₂TPP in CH₂Cl₂ as standard ($\Phi_f = 0.15$) [23] on the basis of the method described by Parker and Rees [24].

2.4. Synthesis and purification of H_2 TPP and H_2 T(2-Me)PP and β -brominated porphyrins

H₂TPP and H₂T(2-Me)PP were prepared and purified according to the Adler et al. method by the reaction of benzaldehyde (3.8 ml, 40 mmol) or 2-methylbenzaldehyde (4.6 ml, 40 mmol) with freshly distilled pyrrole (2.8 ml, 40 mmol) in propionic acid under reflux conditions (30 min) [25]. After washing the precipitates with methanol and water, for further purification, the porphyrins were firstly recrystallized from dichloromethane by the gradual addition of methanol to the solution of the respective porphyrin in dichloromethane. Column chromatography on neutral alumina using dichloromethane gave the product. H₂TPP: UV-Vis in CH₂Cl₂, λ_{max}/nm (logε): 416 (5.79), 513 (4.58), 542 (4.38), 584 (4.30), 644 (4.29). ¹H NMR (400 MHz, CDCl₃, TMS), δ/ppm: -2.71 (2H, br, s, NH), 7.77-7.83 (8H_m and 4H_p, m), 8.26-8.28 (8H_o, dd), 8.90 (8H_{β}, s); H₂T(2-Me)PP: UV-Vis in CH₂Cl₂, λ_{max}/nm (log ϵ): 416 (6.04), 512 (4.74), 545 (4.34), 589 (4.34), 645 (4.25). ¹H NMR (400 MHz, CDCl₃, TMS), δ /ppm: 2.01–2.11 (m, 12H_{Me}), –2.59 (s, 2H, NH), 7.54–7.74 (m, $8H_m$ and $4H_p$), 7.99–8.11 (dd, $4H_o$), 8.70 $(s, 8H_{\beta})$ (see Supplementary material, Fig. S1–S4).

Bromination of H_2TPP was conducted using freshly recrystallized NBS as the bromine source [26–28]. The synthesis and purification of H_2TPPBr_X (X = 2, 4, 6 and 8) performed according to the literature with some modifications. Further details of synthesis, characterization and purification of the brominated porphyrins were described in our recent paper [13].

2.5. Synthesis of H₂TPPBr₂ and H₂TPPBr₄

Direct bromination of H₂TPP with N-bromosuccinamide (NBS) in dried CH_2Cl_2 was used to prepare H_2TPPBr_X (X = 2, 4). Magnetic stirring of the solution of H₂TPP (300 mg, 0.49 mmol) and NBS (180 mg, 0.98 mmol) in 80 ml of dried dichloromethane under reflux conditions for 24 h led to the formation of H₂TPPBr₂. The progress of reaction was monitored by UV-vis spectroscopy at different time intervals. After the required time, an excess amount of NBS was added to complete the dibromination reaction. The shift of the Soret band to higher wavelengths (426 nm) showed the formation of H₂TPPBr₂. In the case of H₂TPPBr₄, 360 mg (1.96 mmol) of NBS was used and the Soret band appeared at 434 nm. The unreacted NBS was removed by washing the product with methanol several times. H₂TPPBr₂ and H₂TPPBr₄ were also recrystallized from CHCl₃/n-hexane (3:1, v/v) for further purification and dried under vacuum. ¹H NMR spectra and CHN elemental analysis were used to confirm the formation of the desired compounds.The degree of bromination of H₂TPP has been determined on the basis of the ratio of the intensities of the signals corresponding to the H_{β} protons and meso-substituents (H_{β}/H_{ortho} and $H_{\beta}/H_{para,meta}$); the formation of H_2TPPBr_2 and H_2TPPBr_4 corresponds to the H_β/H_{ortho} ratios of 0.75 and 0.50 and $H_\beta/H_{\text{para,meta}}$ ratios of 0.50 and 0.33, respectively.

H₂TPPBr₂: UV-Vis in CH₂Cl₂, λ_{max}/nm (logε): 423 (5.55), 520 (4.24), 542 (3.80), 595 (3.69), 650 (3.89). ¹H NMR (400 MHz, CDCl₃, TMS), δ/ppm : 8.78 (m, 6H, β-pyrrole), 8. 5–8.25 (m, 8H, *o*-phenyl), 7.70–7.9 (m, 12H, *m*- and *p*-phenyl), –2.6 (br, 2H, NH) ((see Supplementary material, Fig. S5 and S6). C₄₄H₂₈Br₂N₄.1.85 CH₂Cl₂: Calc C61.66, H 6.23, N 7.15. Found C 62.00, H 6.52, N7.27%.

H₂TPPBr₄: UV-Vis in CH₂Cl₂, λ_{max} /nm (logε): 434 (5.35), 533 (4.03), 613 (3.61), 679 (3.79). ¹H NMR (400 MHz, CDCl₃, TMS), δ/ ppm: 8.55 (m, 4H, β-pyrrole), 8.05–8.25 (m, 8H, *o*-phenyl), 7.70–7.90 (m, 12H, *m*- and *p*-phenyl), -2.5 (2H, H) (see Supplementary material, Fig. S7 and S8). C₄₄H₂₆Br₄N₄ + 0.5 CH₂Cl₂.0.5 H₂O: Calc C 54.44, H 2.87, N 5.71. Found C 50.19, H 2.85, N 5.11%.

The synthesis of H_2 TPPBr₆ and H_2 TPPBr₈ was performed through the reaction of NiTPP (500 mg, 0.75 mmol) and NBS in 1:12 and 1:26 M ratios, respectively. The reaction was conducted in 250 ml dry 1,2-dichlorobenzene under reflux conditions. More details may be found in our recent paper [13] (see (see Supplementary material, Fig. S9 and S10 for the spectra of NiTPP).

H₂TPPBr₆: UV-Vis in CH₂Cl₂, λ_{max}/nm (logε): 454(4.78), 548 (3.50), 607 (3.43), 714 (3.27). ¹H NMR (400 MHz, CDCl₃, TMS), δ/ppm : 8.40 (m, 2H, β-pyrrole), 8.07–8.28 (m, 8H, o-phenyl), 7.70–7.90(m, 12H, *m*- and *p*-phenyl), -1.5 (broad, 2H, NH) (see Supplementary material, Fig. S11–S14 for the spectra of NiTPPBr₆ and H₂TPPBr₆). C₄₄H₂₄Br₆N₄.0.5CH₂Cl₂·0.5H₂OC₆H₁₄: Calc C 56.83, H 4.69, N 4.65. Found C 55.72, H 4.29, N 4.28%.

H₂TPPBr₈: UV-Vis in CH₂Cl₂, λ_{max}/nm (logε): 368, 468(4.81), 565 (3.52), 620 (3.68), 729 (3.40). ¹H NMR (400 MHz, CDCl₃, TMS), δ /ppm: 8.18–8.38 (*m*, 8H, *o*-phenyl), 7.75–7.90 (broad, 12H, *m*- and *p*-phenyl),-1.25 (broad, 2H, NH) (see Supplementary material, Fig. S15–S18 for the spectra of NiTPPBr₈ and H₂TPPBr₈). C₄₄H₂₂Br₈N₄.CH₂Cl₂·H₂O2C₆H₁₄: Calc C 46.83, H 3.65, N 3.90. Found C 44.83, H 3.43, N 3.52%.

Synthesis of H₂T(2-Me)PPBr₄:The synthesis of H₂T(2-Me)PPBr₄ has been carried out by direct bromination of H₂T(2-Me)PP (328 mg, 0.49 mmol) with NBS (360 mg, 1.96 mmol) in dried CH₂Cl₂ (80 ml) under reflux conditions (see the synthesis of H₂TPPBr₄) [13,25,27,28].

H₂T(2-Me)PPBr₄: UV-Vis in CH₂Cl₂, λ_{max} /nm: 426, 582, 659; ¹H NMR (400 MHz, CDCl₃, TMS), δ/ppm: –2.59 (2H, br, s, NH), 7.54–7.74 (8H_m and 4H_p, m), 7.99–8.11 (4H_o, dd), 8.70 (4H_β, s),2.01–2.11(12H_{Me}, m) (see Supplementary material, Fig. S19 and S20).

2.6. Porphyrin diprotonated species

Porphyrin dications with CF₃COOH and CH₂ClCOOH were synthesized and purified by addition of excess amounts (beyond the 2:1 M ratio of acid to porphyrin) of the respective acid to the solution of porphyrin in dichloromethane. Slow evaporation of the solvent and excess acid at room temperature gave the corresponding dications. The UV-Vis and ¹H NMR spectra of the dications are presented in the (see Supplementary material, S21-S28 and S29-S36.

H₄TPPBr₂(CF₃COO)₂: ¹H NMR (400 MHz, CDCl₃, TMS), δ/ppm: 0.5 (s, br, 4H, NH), 8.2-8. 75 (m, 6H, β-pyrrole), 8.2-8.75 (m, 8H, o-phenyl), 7.9-8.02 12H, *mp*-phenyl). (m, and H₄TPPBr₂(CH₂ClCOO)₂: ¹H NMR (400 MHz, CDCl₃, TMS), δ/ppm: 0.5 (S, br, 4H, NH), 8.25-8. 70 (m, 6H, β-pyrrole), 8.25-8.70 (m, 8H, o-phenyl), 7.9-8.15 (m, 12H, m- and p-phenyl). H₄TPPBr₄(CF₃-COO)₂: ¹H NMR (400 MHz, CDCl₃, TMS), δ/ppm: 0.0 (4H, H), 8.2–8.7 (m, 4H, β-pyrrole), 8.2–8.7 (m, 8H, o-phenyl), 7.9–8.01 (m, 12H, mand *p*-phenyl). H₄TPPBr₄(CH₂ClCOO)₂: ¹H NMR (400 MHz, CDCl₃, TMS), δ/ppm:0-1(4H, H), 8.2-8.65 (m, 4H, β-pyrrole), 8.2-8.65 (m, 8H, o-phenyl), 7.9–8.10 (m, 12H, m- and p-phenyl). H₄TPPBr₆ (CF₃COO)₂: ¹H NMR (400 MHz, CDCl₃, TMS), δ/ppm: 0–1 (broad, 4H, NH),8.35–8.65 (m, 2H, β-pyrrole), 8.35–8.65 (m, 8H, *o*-phenyl), 7.90–8.05(m, 12H, *m*- and *p*-phenyl). H₄TPPBr₆(CH₂ClCOO)₂: ¹H NMR (400 MHz, CDCl₃, TMS), δ/ppm: 0.9 (broad, 4H, NH),8.45–8.8

(m, 2H, β-pyrrole), 8.45–8.8 (m, 8H, *o*-phenyl), 7.90–8.1(m, 12H, *m*-and *p*-phenyl). H₄TPPBr₈(CF₃COO)₂: ¹H NMR (400 MHz, CDCl₃, TMS), δ/ppm: 0.5 (broad, 4H, NH). 8.45–8.85 (d, J, 8.52, 8H, *o*-phenyl), 7.65–8.28 (broad, 12H, *m*- and *p*-phenyl).H₄TPPBr₈(CH₂ClCOO)₂: ¹H NMR (400 MHz, CDCl₃, TMS), δ/ppm: 0.5 (broad, 4H, NH), 8.5–8.8 (d, J, 8, 8.52, 8H, *o*-phenyl), 7.85–8.15 (broad, 12H, *m*- and *p*-phenyl).

3. Results and discussion

3.1. Absorption spectra of porphyrins

The UV-Vis spectral data of H₂TPP and the brominated porphyrins are summarized in Table 1. It is observed that the Soret and Q bands of the brominated porphyrins are red shifted (6-51 and 3-82 nm, respectively) with respect to those of the corresponding bands of H₂TPP. Porphyrinic photosensitizers with red shifted absorption bands are of major interest from energy consumption and application points of view; penetration of light through a turbid medium in tumour tissue is of vital importance in photodynamic therapy. It was found that the best penetration of light through tissue is observed at wavelengths in the range of 700–1000 nm, the so-called therapeutic window [29]. As seen from Table 1, the Q(0,0) bands of H_2TPPBr_6 and H_2TPPBr_8 appear in the wavelength region higher than 700 nm. In other words, the β bromination of porphyrins is an efficient approach to shift the absorption bands towards the therapeutic window. Also, the brominated porphyrins have significantly decreased fluorescence quantum yields that facilitates the non-radiative S₁ to T₁ intersystem crossing, needed for the activation of molecular oxygen [15].

3.2. Photooxidation with H_2 TPPBr_x

In order to investigate the catalytic activity of the brominated porphyrins, H_2 TPPBr_x were used as photosensitizers for the oxidation of olefins.

3.3. Optimization of the reaction conditions

The optimized reaction conditions including the molar ratio of porphyrins to olefin, solvent and light source were investigated (Tables 2-4). As was shown in elsewhere, [30] the use of acetonitrile and toluene in 1:9 ratio is the best solvent mixture for conducting the oxidation reactions. In order to meet the requirement of green chemistry, the reactions were also conducted in a 10:9:1 mixture of water, acetonitrile and toluene. Interestingly, this change led to a remarkable increase in the conversion value for the reaction catalyzed by H_2 TPPBr₂ (Table 2). Under these conditions, the best catalyst:olefin molar ratio for achieving the maximum conversion was the 1:1000 one (Table 3). It is noteworthy that again the maximum TON values were obtained at the 1:10000

In the 1:1 acetonitrile to toluene mixed solvent, there was no large difference between the conversion values obtained in the 1:1000 to 1:10000 catalyst to olefin molar ratio (Table 2, i), however a turnover number of 3300 was achieved using the latter that was much higher than that observed at the other molar ratios.

The type of light source plays crucial role in the efficiency of the porphyrinic photosensitizers. In a recent work, [30] it was found that 10 W blue and white LED lamps are more efficient than a red LED lamp in the photooxidation catalyzed by porphyrin diacids. Also, the minimum extent of catalyst degradation was observed in the case of the white LED lamp. As seen from Table 4, the use of a 10 W white LED lamp led to an increase in the conversion value, although similar degrees of catalyst degradation were observed in the case of the white and blue LED lamps.

3.4. Optical properties of H₂TPPBr_x

Porphyrin derivatives with red shifted absorption bands are of interest for applications such as activation of molecular oxygen and PDT. However, deactivation of the excited state through fluorescence emission decreases the efficiency of porphyrin sensitizers in formation of T₁ excited state and consequently singlet oxygen. Accordingly, a decrease in the rate of radiative decay of the S₁ excited state and fluorescence quantum yield (ϕ_f) is expected to increase the rate of non-radiative decay of the excited state which is one of the requirements of an efficient sensitizer. The optical properties of the brominated porphyrins summarized in Table 6 is in agreement with significant decrease in radiative rate constant (k_r) upon the bromination of H₂TPP. However, the non-radiative rate constants (knr) were greater or comparable with that of H_2 TPP. Also, ϕ_f values of 0.073 and 0.000027 were estimated for H₂T(2-Me)PP [31] and H₂T(2-Me)PPBr₄, respectively. Furthermore, bromination of $H_2T(2-Me)PP$ decreases both k_r and k_{nr} values from 0.48 and 0.33 to 0.0021 and 0.25 ($\times 10^{-6} \text{ s}^{-1}$), respectively. These observations are probably due to the heavy atom effect caused by the introduction of bromine atoms at the porphyrin periphery.

3.5. The comparison of H_2 TPPBr_x compounds

The bromination of H_2 TPP at the β positions leads to the appearance of the absorption bands of the aromatic macrocycle at higher wavelengths. Also, the distribution of electron-density over the aromatic macrocycle is influenced by the presence of the electronegative bromine atoms at the porphyrins periphery. The latter is expected to tune the oxidative stability of the photosensitizer.

The results for the oxidation of cyclooctene catalyzed by different H_2TPPBr_x compounds in the presence of a 10 W white LED lamp are summarized in Figs. 2 and 3 and Table 7. It is observed that in different reaction times (up to 72 h) and various catalyst to olefin molar ratios (1:1000 to 1:10000), H_2TPPBr_2 and H_2TPPBr_4 were much more efficient that the other brominated porphyrins. Also, in a reaction time of 24 h, H_2TPPBr_2 was more stable than the other ones towards oxidative degradation. However, at longer reaction times, the hexa and octa-brominated porphyrins suffer

Table 1
UV-Vis spectral data of H_2 TPPBr _x in dichloromethane.

Porphyrin	Soret λ/nm	IV λ/nm	III λ/nm	II λ/nm	I λ/nm
H ₂ TPP	417	514	548	589	647
$(\log \epsilon, M^{-1} cm^{-1})$	(5.79)	(4.58)	(4.38)	(4.30)	(4.29)
H ₂ TPPBr ₂	423	520	542	595	650
(loge)	(5.55)	(4.24)	(3.80)	(3.69)	(3.89)
H ₂ TPPBr ₄	434	-	533	613	679
(logɛ)	(5.35)		(4.03)	(3.61)	(3.89)
H ₂ TPPBr ₆	454	-	548	607	714
(logɛ)	(4.78)		(3.50)	(3.43)	(3.27)
H ₂ TPPBr ₈	468	-	565	620	729
(loge)	(4.81)		(3.52)	(3.68)	(3.40)

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Table 2

Effect of solvent on the photooxidation of cyclooctene. ^a
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Porphyrin	solvent	Conversion ^{b,c} (%)	TON (TOF, h ⁻¹) ^{d,e}	Catalyst degradation (%) ^f
H ₂ TPPBr ₂	1:9 ^g 1:1 ^h 1:1 ⁱ	26 18 33	260 (4) 180 (2) 3500 (45)	76 73 77
	10:9:1 ^j	70	700 (10)	100

^aPorphyrin and olefin were used in a 1:1000 molar ratio. A 10 W blue LED lamp was used as the light source. ^b Based on GC analysis, for a reaction time of 72 h. ^c The product was also characterized by ¹³C NMR by conducting the oxidation reaction in CCl₄. ^d TON demonstrates the number of moles of the product obtained per one mole of the catalyst. ^eTOF shows the turnover number of the reaction per time unit. ^f On the basis of the change in the absorbance at the λ_{max} of the porphyrin. ^{g,h,i}toluene:CH₃CN. ⁱ For a 1:10000 molar ratio of porphyrin to olefin. ^j H₂O:CH₃CN:toluene.

Table 3

Catalyst:olefin	Conversion (%)	TON (TOF, h^{-1})	Catalyst degradation (%)
1:1000	80	800 (11)	100
1:5000	30	1600 (22)	94
1:10000	17	1700 (24)	100

^aSee the footnotes of Table 1.

^bIn H₂O:CH₃CN:toluene (10:9:1) mixed solvent.

Table 4

Photooxidation of cyclooctene using different LED lamps.^{a,b}

LED lamp	Conversion (%)	TON (TOF, h^{-1})	Degradation (%)
Blue (10 W)	70	700(10)	100
White (10 W)	80	800(11)	100

^a See the footnotes of Tables 1 and 2.

Table 5

Photooxidation of cyclooctene catalyzed by $H_2T(2\mbox{-}Me)PPBr_4$ in $H_2O:CH_3CN:toluene~(10:9:1).^a$

Porphyrin	Conversion (%)	TON(TOF, h^{-1})	Catalyst degradation (%)
H ₂ T(2-Me) PPBr₄	32 ^b	320 (4)	75
-	36 ^c	360 (5)	76

^aSee the footnotes of Tables 1 and 2. ^{b,c} Under the irradiation with 10 W white and blue LED lamps, respectively.

from extensive oxidative degradation. In other words, while the di and tetra-brominated porphyrins were almost as stable as H₂TPP, the hexa and octa- brominated ones were dramatically less stable towards oxidative degradation than their non-brominated counterpart. According to the four orbital model of porphyrins [37]. for porphyrin HOMO and HOMO-1 (a_{2u} and a_{1u} , respectively), the electron densities are largest on the meso and α carbons, respectively and therefore these positionsare more

susceptible to oxidative degradation through electrophilic attack by the reactive oxygen species (ROS) [38–41]. Furthermore, Dolphin et al., reported a novel stepwise oxidative degradation at the β position of Ni(II) porphyrins which was mentioned as a novel to the field of porphyrin chemistry [42]. The increased coplanarity of the meso phenyl groups and porphyrin core leading to increased electron-donation to the porphyrin core, the weakening of different bonds of H2TPPBrx relative to those of H2TPP, destabilized HOMO of the substantially distortedH₂TPPBr₆ and H₂TPPBr₈predicted from the DFT calculations [13,43], and the decreased ring current and the resonance energy of the brominated porphyrins caused by the out-of-plane distortion of the aromatic macrocycle may be used to explain the increased oxidative degradation of the higher degrees of the brominated porphyrins. The latter was deduced from the upfield shift of the β protons of the brominated porphyrins with respect to those of H₂TPP [13,44,45].Recently, we have shown that the distribution of electron density on different atoms of the aromatic macrocycle calculated by DFT calculation, cannot properly explain the order of oxidative stability of a series of porphyrin derivatives and other parameters such as dihedrdal angles between the meso aryl substituents and porphyrin mean plan and the energy of the frontier orbitals of the aromatic macrocycle may be used to rationalize the point [46].

3.6. Substitution of phenyl group with a bulky substituent

The introduction of bulky substituents at the meso positions of metalloporphyrins has been used as an efficient strategy to overcome their oxidative degradation [47–49]. To evaluate the efficiency of this approach in decreasing the oxidative degradation

Table 6

Fluorescence quantum yields and the rate constants for radiative and non-radiative relaxation of H2TPPBrx estimated from their absorption and emission spectra.

Free base porphyrins	H ₂ TPP	H ₂ TPPBr ₂	H ₂ TPPBr ₄	H ₂ TPPBr ₆	H ₂ TPPBr ₈
5(0,0)					
Φ_f^a	0.13	0.00106	0.00048	0.00345	0.002760
$\tau_1 (ns)^b$	409	536	351	683	842
$\tau_2 (ns)^c$	464	520	359	826	1225
$\tau_3 (ns)^d$	466	600	377	732	742
$K_{r1} (\times 10^{-6} \text{ s}^{-1})^{e}$	0.32	0.0019	0.0014	0.0051	0.0032
$K_{r2} (\times 10^{-6} \text{ s}^{-1})^{\text{f}}$	0.28	0.0020	0.0013	0.0042	0.0023
$K_{r3} (\times 10^{-6} \text{ s}^{-1})^{g}$	0.28	0.0017	0.0013	0.0047	0.0037
$K_{nr1} (\times 10^{-6} s^{-1})^{h}$	2.1	1.9	2.9	1.5	1.2
K_{nr2} (×10 ⁻⁶ s ⁻¹) ⁱ	1.9	1.9	2.8	1.2	0.81
$K_{nr3} (\times 10^{-6} s^{-1})^{j}$	1.9	1.7	2.6	1.4	1.3

^aBased on a reported value of 0.13 for $\phi_{F}of H_2TPP$ in CH₂Cl₂ [32].^b $\tau_1^{-1} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v^2 \rangle \int \varepsilon(v) dv$. $c_{\tau_2^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \int \frac{(2v_0 - v)^3}{v} \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $c_{\tau_2^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \int \frac{(2v_0 - v)^3}{v} \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $c_{\tau_2^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \int \frac{(2v_0 - v)^3}{v} \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{\frac{g_{L}}{g_{u}}}^{2g_{L}} \langle v_f^2 \rangle \int \varepsilon(v) dv$. $d_{\tau_3^{-1}} = 2.880 \times 10^{-9} n_{$

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Fig. 2. Photooxidation of cyclooctene in the presence of different molar ratios of olefin: H₂TPPBr_x molar ratios under the irradiation of a white LED lamp (10 W) In H₂O: CH₃CN:toluene (10:9:1) mixed solvent.



Fig. 3. Photooxidation of cyclooctene under the irradiation of a blue LED lamp (10 W).

of the brominated porphyrins, the β -tetra-brominated derivative of *meso*-tetra(2-methylphenyl)porphyrin, H₂T(2-Me)PPBr₄ was prepared and its photocatalytic performance was studied (Table 5). The comparison of the results summarized in Table 5 and those of H₂TPP (Figs. 2, 3 and 4, Table 7) and H₂T(2-Me)PP(Table 7, entries 11 and 12) shows that the presence of methyl substituents at the ortho position of the non-brominated porphyrin, leads to a ca. 10–15% increase in the conversion value. Also, significant decrease of catalyst degradation (ca. 40 to 60%) was observed (see entries 1, 2, 11 and 12, Table 7). Interestingly, the introduction of four bromine atoms decreased the photocatalytic activity by 31 to 53% relative to that of H₂TPPBr₄ under the same conditions. Instead, a remarkable decrease (30 to 50%) in oxidative degradation was observed (see entries 5,6,13 and 14).

3.7. Singlet oxygen quantum yields

The efficiency of photosensitizers in light absorption to convert ${}^{3}O_{2}$ into singlet oxygen, known as Φ_{Δ} is as an important parameter to evaluate the efficiency of novel photocatalysts [21].The changes in the absorption spectrum of DPBF in the presence of the photosensitizers in dichloromethane are shown in Fig. 4. The Φ_{Δ} values (Table 8) of H₂TPPBr_x determined by using H₂TPP as a reference photosensitizer and DPBF as a specific singlet oxygen quencher, [20] decrease as H₂TPPBr₂ > H₂TPPBr₄ \gg H₂TPPBr₆ > H₂TPPBr₈. The correlation observed between the photocatalytic activity of H₂TPPBr_x and their Φ_{Δ} is in accord with the involvement of singlet oxygen as the main ROS in this reaction. It is noteworthy that the addition of 1,4-benzoquinone as the scavenger of superoxide anion

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Table 7
Oxidation of cyclooctene catalyzed by H ₂ TPP, H ₂ T(2-Me)PP, H ₂ TPPBr _x and H ₂ T(2-Me)PPBr ₄ under the optimized reaction conditions. ^a

Entry	Photosensitizer	LED lamp	Time (h)	Conversion (%)	TON (TOF, h^{-1})	Degradation (%)
1	H ₂ TPP	White	72	71	3550 (49.3)	82
2	H ₂ TPP	Blue	72	74	3700 (51.3)	82
3	H_2TPPBr_2	White	72	30 (80) ^b	1500 (20.8) 800 ^b (11.1) ^b	94 (1 0 0) ^b
4	H_2TPPBr_2	Blue	72	32 (70) ^b	$1600(22.2)700^{b}(9.7)^{b}$	$94(100)^{b}$
5	H ₂ TPPBr ₄	White	72	13 (70) ^b	$650 (9.0) 700^{b} (9.7)^{b}$	$100(100)^{b}$
6	H ₂ TPPBr ₄	Blue	72	13 (45) ^b	$650 (9.02) 450^{b} (6.2)^{b}$	100 (1 0 0) ^b
7	H_2TPPBr_6	White	6	4 ^b	40 (4.0)	91
8	H ₂ TPPBr ₆	Blue	6	8 ^b	80 (13.3)	100
9	H ₂ TPPBr ₈	White	6	6 ^b	60 (10.0)	95
10	H ₂ TPPBr ₈	Blue	6	6 ^b	60 (10.0)	89
11	H ₂ T(2-Me)PP	white	72	80 ^b	800 (11.1)	40^{b}
12	H ₂ T(2-Me)PP	Blue	72	79 ^b	790 (11.0)	18 ^b
13	H ₂ T(2-Me)PPBr ₄	White	72	17 ^b	170 (2.4)	70 ^b
14	H ₂ T(2-Me)PPBr ₄	Blue	72	14 ^b	140 (1.9)	50 ^b

 a Toluene and CH₃CN were used in 9:1 ratio; photocatalyst and olefin were used in 1:5000.

^b Porphyrin and olefin were used in a 1:1000 M ratio.



Fig. 4. The change in the UV-Vis spectrum of DPBF upon irradiation with a 10 W red LED lamp in the presence of the brominated porphyrins and H₂TPP. The change in the absorption bands estimated through the measurement of the area of the band at different time intervals is only due to the change in the absorption of the corresponding band of DPBF; control reactions showed that all the photosensitizers are completely stable against photooxidative degradation up to ca. 2 h.

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Singlet oxygen quantum yield of the brominated compounds in dichloromethane.^a

Entry	Photosensitizer	Φ_{Δ}
1	H_2 TPP	0.70
2	H_2 TPPB r_2	0.21
3	H_2 TPPB r_4	0.13
4	H_2 TPPB r_6	0.04
5	H ₂ TPPBr ₈	0.02
6	H ₂ T(2-Me)PP ^b	0.51
7	H ₂ T(2-Me)PPBr ⁶	0.31

Singlet oxygen quantum yields, determined using a 10 W red LED lamp and DPBF as a quencher of singlet oxygen and H2TPP as a reference photosensitizer.^{b,c} See Figs. S4 and S20 for the UV-Vis spectra.

radical [14,18,30] has no effect on the conversion of cyclooctene to cyclooct-1-en-3-yl hydroperoxide which is in agreement with the absence of this species as ROS in the catalytic cycles.

3.8. Brominated porphyrins versus the non-brominated counterparts

The photocatalytic activity of the brominated porphyrins was also compared with that of the non-brominated porphyrins, H₂TPP and H₂T(2-Me)PP (Table 7). It is observed that while the partially brominated porphyrins, H₂TPPBr₂ and H₂TPPBr₄, are more efficient photosensitizers than H₂TPPBr₆ and H₂TPPBr₈, (entries 3-10) under the optimized reaction conditions, the former has no advantage over H₂TPP. Also, the brominated porphyrins show higher degrees of catalyst degradation compared to that of H_2 TPP. In spite of the comparable catalytic activity of H_2 T(2-Me) PP and H₂TPP (entries 1, 2, 11 and 12), the former has a remarkably higher oxidative stability than the former. In other words, the increased steric hindrance at the meso position is in favor of increasing the stability of photocatalyst. On the other hand, H₂T (2-Me)PPBr₄ was much less efficient and less stable than the non-brominated porphyrin (entries 11–14). As seen from Table 8, a decrease in ϕ_{Δ} value (Table 8) was observed upon the bromination of H₂T(2-Me)PP which is in accord with the decrease catalytic performance of the brominated porphyrin.

3.9. Effect of weak and strong acids

As seen from Tables 2–5 and Table 7, the brominated porphyrins, especially those with 6 and 8 bromine atoms, suffer from high degrees of degradation under the reaction conditions. Recently, we have shown that the oxidative degradation of porphyrin photosensitizers may be altered by using their dications with weak and strong acids [14,19,22,30]. Accordingly, the oxidation reactions were conducted in the presence of the diacids of the brominated porphyrins (Fig. 5). The oxidative degradation of the brominated porphyrins was significantly decreased upon the formation of dication with chloroacetic acid. Furthermore, the porphyrin dications were generally more efficient photosensitizers than their corresponding free base counterparts. In this regard the conversion values achieved in the presence of the dications of H₂TPPBr₆ and H₂TPPBr₈ were much more than those obtained in the presence of the free base porphyrins. It is noteworthy that H₂TPPBr₆ and H₂TPPBr₈ showed the photocatalytic activity among the series of the free base brominated porphyrins (Figs. 2 and 3, Table 7). As was reported previously [14], weak carboxylic acids are usually more efficient than strong acids in decreasing the oxidative degradation of porphyrins (see Fig. 6).

The absorption spectra data of the dications of H_2TPPBr_x with CF₃COOH and CH₂ClCOOH are summarized in Table 9. The formation of porphyrin diacids is associated with the red shift of the Soret and Q bands. Also, the four Q bands of the free base porphyrins decrease to one or two bands corresponding the Q(0,0) and Q(0,1) bands, due to the change in the symmetry of the porphyrin core [14,50,51]. Accordingly, the dications of the brominated porphyrins, may be considered as more efficient, more stable and highly red shifted analogues of H_2TPPBr_x . Also, diprotonation of H_2TPPBr_x is an efficient strategy to overcome the extensive oxidative degradation of these photosensitizers.

The comparison of data evaluated from Figs. 4 and 6 (Tables 8 and 9) shows a remarkable (2.5 to 6 fold) increase in the ϕ_{Δ} value caused by protonation of H₂TPPBr_x which is more pronounced in the case of the hexa and octa-brominated porphyrins. The significantly greater ϕ_{Δ} and oxidative stability of the diprotonated compounds of the brominated porphyrins provide a reasonable explanation for the observed improved photocatalytic performance of the brominated porphyrins induced by the protonation of the aromatic macrocycles. Also, in the series of the diprotonated species (Table 9), ϕ_{Δ} decreased continuously from the diacids of H₂TPPBr₂ to those of H₂TPPBr₈. This result is clearly in accord with the higher photocatalytic activity of diprotonated species of H₂TPPBr₂ and H₂TPPBr₄. Furthermore, the diprotonated



Fig. 5. Oxidation of cyclooctene in the presence of H₂TPPBr_x and their dications with CF₃COOH (TFA) and CH₂ClCOOH (CAA) under the optimized reaction conditions (see the footnotes of Table 7); H₄TPPBr₂(CH₂ClCOO)₂ and H₄TPPBr₂(CF₃COO)₂ were the most stable and most efficient photosensitizers of the series, respectively.

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Fig. 6. The change in the UV-Vis spectrum of DPBF upon irradiation with a 10 W red LED lamp in the presence of the diprotonated species of H₂TPPBr_x with CF₃COOH and CCH₂ClCOOH.

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Table 9

UV-Vis spectral data, Φ_{Δ} and Φ_f of the dications of H₂TPPBr_x with CF₃COOH and CH₂ClCOOH in dichloromethane.^a

Porphyrin	Soret λ/nm	Q(0,0) λ/nm	$\Phi_{\Delta}{}^{b}$	Φ_{f}	$K_r (\times 10^{-6} s^{-1})^c$	$K_{nr1} \ (\times 10^{-6} \ s^{-1})^d$
H ₄ TPPBr ₂ (CF ₃ COO) ₂	451	674	0.59	0.00516	15.32	15.22
$(\log \epsilon, M^{-1} cm^{-1})$	(5.43)	(4.66)				
$H_4TPPBr_2(CH_2CICOO)_2$	453	678	0.49	0.00678	14.73	14.60
(logɛ)	(5.30)	(4.49)				
$H_4TPPBr_4(CF_3COO)_2$	462	696	0.34	0.00203	9.92	9.90
(logɛ)	(5.32)	(4.43)				
$H_4TPPBr_4(CH_2ClCOO)_2$	467	696	0.30	0.00187	11.93	11.90
(logɛ)	(5.21)	(4.38)				
$H_4TPPBr_6(CF_3COO)_2$	483	725	0.10	0.00248	2.36	2.35
(logɛ)	(4.84)	(4.08)				
$H_4TPPBr_6(CH_2ClCOO)_2$	483	725	0.14	0.00304	3.65	3.64
(logɛ)	(4.84)	(4.13)				
$H_4TPPBr_8(CF_3COO)_2$	491	747	0.16	0.00180	2.57	2.56
(logɛ)	(4.93)	(4.74)				
$H_4TPPBr_8(CH_2ClCOO)_2$	490	743	0.12	0.00267	3.33	3.32
(logɛ)	(4.97)	(4.23)				

^a See the footnotes of Table 6 and 8 for more details.

^b Measured through the reaction of singlet oxygen with DPBF (Fig. 6). ^cAverage of K_{r1}, K_{r2} and K_{r3}. ^dAverage of K_{nr1}, K_{nr2} and K_{nr3}

Table 10 Photooxidation of cyclohexene catalyzed by the diprotonated derivatives of H_2TPPBr_2 .^a

Photosensitizers	Conversion (%)	Time (h)	Degradation (%)
H ₂ TPPBr ₂ (CH ₂ ClCOOH) ₂	69	72	15
$H_2TPPBr_2(CF_3COOH)_2$	73	72	82

^a See the footnotes of Table 1. A 10 white LED lamp was used as the light source.



Fig. 7. Proposed mechanism for the formation of 2-cyclohexene-1-one from cyclohexene-3-hydroperoxide.

compounds of the weaker acid (CH₂ClCOOH), showed higher ϕ_{Δ} compared to those of CF₃COOH. On the other hand, the ϕ_F of H₂TPPBr_x (Table 6) and their diprotonated species (Table 9) revealed an increased fluorescence quantum yield in the case of the di- and tetra-brominated porphyrins but a decreased one in the case of the hexa- and octa-brominated porphyrins. Also, both the K_r and K_{nr} values (Table 9) of the diprotonated species decreases from H₂TPPBr₂ to those of H₂TPPBr₈. In comparison with the data summarized in Table 6, the diprotonated porphyrins have K_r and K_{nr} values greater than those of the free base porphyrins which may be also used to explain higher ϕ_{Δ} values of the former.

3.10. Photooxidation of cyclohexene

The oxidation of cyclohexene in the presence of the dications of H_2 TPPBr₂ as the best photosensitizers of the series was conducted (Table 10). As was reported previously [52], the oxidation of cyclohexene gives 2-cyclohexene-1-one as the sole product (see supplementary material for further details). Also, cyclooctene shows a higher reactivity compared to that of cyclohexene. The formation of 2-cyclohexene-1-one in the case of cyclohexene may be explained on the basis of the decomposition of the corresponding

alkyl hydroperoxide (Fig. 7). However, a ca. 15% decrease in the oxidative degradation of the photosensitizers was observed in the oxidation of cyclohexene.

4. Conclusion

Aerobic oxidation of cyclooctene in the presence of H₂TPPBr_x was studied and found that: (i) H₂TPPBr₂ and H₂TPPBr₄ showed the highest photocatalytic activity among the series of brominated porphyrins; (ii) a close correlation was observed between the photocatalytic activity of the brominated porphyrins and their singlet oxygen quantum yield; (iii) H₂TPPBr_x compounds showed remarkably decreased fluorescence quantum yields and radiative decay rate constants relative to those of H₂TPP; (iv) although the former presented a two-fold higher catalytic activity than the latter during the first 24 h of the reaction, they showed a comparable catalytic activity by continuing the reaction for a longer time (48 to 72 h); (v) with the exception of H₂TPPBr₂ and H₂TPPBr₄, the other brominated porphyrins suffered from high degrees of oxidative degradation upon the photooxidation reaction; (vi); the sterically hindered β-brominated porphyrin, H₂T(2-Me)PPBr₄ with bulky methyl substituents at the ortho positions demonstrated an improved oxidative stability (30 to 50%) in comparison with H₂TPPBr₄ at the cost of significant loss of photocatalytic activity. It is noteworthy that H₂T(2-Me)PP was much more stable than H₂TPP during the oxidation reaction; (*vii*) protonation of the brominated porphyrins with CF₃COOH and CH₂ClCOOH led to a remarkable increase in their oxidative stability which was more pronounced in the case of the latter; (viii) the ϕ_{Δ} of the diprotonated counterparts of H_2TPPBr_x is significantly higher than that of H₂TPPBr_x which is in accord with the higher catalytic performance of the former. Also, the diprotonated compounds with lower degrees of β-bromination have larger ϕ_{Δ} than the non-protonated H₂TPPBr_x; (*ix*) the formation of porphyrin diacids, shifted the absorption bands in the Soret and Q band regions towards longer wavelengths with respect to those of H_2 TPPBr_x; (x) the significantly improved photocatalytic performance of the diprotonated H₂TPPBr_x is mainly due to the increased oxidative stability and singlet oxygen quantum yield of the brominated porphyrins induced by the weak and strong carboxylic acids.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.10.005.

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