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Photocatalytic activity of the molecular complexes of meso-tetraarylporphyrins with Lewis acids for the oxidation of olefins: Significant effects of Lewis acid and meso substituent

Aida G. Mojarrad[a] and Saeed Zakavi*[a]

Dedicated to Prof. Dr. Daryoush Mohajer on occasion of his 78th birthday

Abstract: In continuing our studies on the photosensitizing ability of the 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) molecular complex of meso-tetraphenylporphyrin H_2TPP, in the present study the photocatalytic activity of tetra-cyanoethylene (TCNE) molecular complexes of a series of para or ortho substituted meso-tetraarylporphyrins (aryl = phenyl, 2-methylphenyl, 4-methylphenyl and 4-methoxylphenyl) for the areobic oxidation of olefins has been studied and compared with that of the DDQ counterparts and the free base porphyrins. Significantly higher catalytic performances were observed for the TCNE molecular complexes in a much shorter reaction time. This observation is in accord with the remarkably greater singlet oxygen quantum yield of the TCNE complexes ($φ_Δ$ = 0.57-0.98) relative to that of the DDQ complexes ($φ_Δ$ = 0.03-0.57) and the free base porphyrins (0.32-0.63). Also, the photocatalytic activity of the molecular complexes was found to be greatly influenced by the meso substituents. The involvement of a singlet oxygen mechanism in the oxidation reactions was confirmed by using 1,3-diphenylisobenzofuran and 1,4-benzoquinone as the singlet oxygen quencher and superoxide anion radical scavenger, respectively.

Introduction

Synthesis of new porphyrin-based photosensitizers with the aim of increasing the photocatalytic activity of commonly used porphyrinic systems has been the subject of many studies in recent years[1]. The chemically and photochemically activated forms of molecular oxygen namely superoxide, peroxide, singlet oxygen and high valent metal oxo species have versatile applications in a wide range of areas[2] containing the photodynamic cancer therapy (PDT), fine chemical syntheses and wastewater treatment. However, most porphyrin-based photosensitizers suffer from oxidative instability under the reaction conditions. On the other hand, the porphyrins with red shifted absorption bands in the visible region are of great importance from the biomedical application point of view[3]. The increase in the oxidative stability of these macrocyclic compounds necessitates the synthesis of porphyrins with electron-deficient and/or bulky substituents at the porphyrin periphery. It usually requires difficult multistep synthetic methods and/or expensive substituted pyrroles and aldehydes[4]. It is well-established that porphyrin core can be readily substituted at the center of the macrocycle by various protic or Lewis acids[5]. This involves a two electron donation from the pyrrolenine nitrogen atoms to the acid molecule and therefore the formation of porphyrin diprotonated species and molecular complexes is accompanied with a decrease in the electron density on the aromatic macrocycle. In other words, a wide range of core substituted electron-deficient porphyrins may be synthesized by this approach as novel alternatives to the β and substituted porphyrins. Also, the formation of the adducts between porphyrins and different σ and /or π acceptors induces meso remarkable conformational and spectral changes[6]. The net effect of these changes was found to be the red shift of the Soret and Q bands of porphyrins[6b, 6c]. Accordingly, this approach may be utilized to prepare porphyrin-based compounds with significantly red shifted absorption bands at the visible region due to the saddle conformation of the aromatic macrocycle and the decreased dihedral angle between the meso aryl substituents and the porphyrin mean plane.

Over the past decades, the adduct formation of porphyrins with 4,6-dinitrobenzofuroxane[7], 2,4,5,7-tetra-nitrofluorenone[8], 3-acetylpyridine[9], 3-cyanopyridine[10], 3-picoline[11], 1-methylimidazole[12], propylene oxide[13], 1,4-naphthoquinone[14], 4-nitrophenol[15], cyclodextrin derivatives[16], 7,7,8,8-tetracyanoquinodimethane (TCNQ)[17], 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[6b] and tetra-cyanoethylene (TCNE)[6c] was reported. However, no attention was paid to the potential photosensitizing ability of these donor-acceptor molecular complexes. Very recently, we have reported that the photocatalytic activity and oxidative stability of *meso*-tetraphenylporphyrin (H_2TPP) remarkably increased upon adduct formation with DDQ[18]. In the present study, the TCNE molecular complexes of a series of para or ortho substituted *meso*-tetraarylporphyrins (Figure 1) have been used as photosensitizer in the aerobic oxidation of olefins. In spite of the fact that in both the TCNE and DDQ adducts, the cyano groups were considered as the acceptors[6b, 6c], the former showed a

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significantly higher catalytic performance and reaction rates relative to the latter. This observation is consistent with the significantly enhanced singlet oxygen quantum yield (φ_{Δ}) of the TCNE complexes. Moreover, the influence of the steric effects of the acceptor molecules in the rate of the oxidation reactions may be also involved. Also, the effect of meso substituents on the catalytic activity and oxidative stability of the TCNE and DDQ adducts was investigated. It is noteworthy that the solubility of porphyrins in solvents such as acetonitrile remarkably increased upon molecular complexation with DDQ and TCNE.

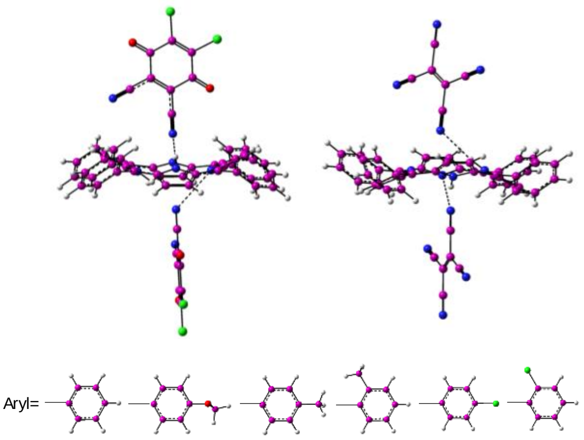


Figure 1. The proposed structure of DDQ and TCNE molecular complexes of meso-tetra(aryl) porphyrins; Aryl= phenyl, 4-methoxyphenyl, 4-methylphenyl, 2-methylphenyl, 4-chlorophenyl and 2-chlorophenyl [6b,6c].

Results and Discussion

Different parameters influence the catalytic activity of porphyrin derivatives. Also, the stability of the catalyst under oxidative conditions is determined by the steric and electronic properties of the peripheral substituents. In order to achieve the optimized conditions of the photooxidation reactions, various molar ratios of catalyst to substrate, light sources and porphyrins were examined.

Photooxidation of cyclooctene

Aerobic photooxidation of cyclooctene catalyzed by $H_2TPP(TCNE)_2$ gave cyclooct-1-en-3-yl hydroperoxide as the major product. The reaction was conducted using different molar ratios of catalyst:olefin (Figure 2) and the maximum conversion and TON values were achieved in the 1:2000 molar ratio for a reaction time of 24 h. Furthermore, the change in the absorption at the λ_{max} of the molecular complex (440 nm) was used to measure the oxidative stability of $H_2TPP(TCNE)_2$ under the reaction conditions.

The oxidative degradation of the catalyst may be considered as an undesired reaction that competes with the main oxidation reaction. Accordingly, the increase in the catalyst:substrate molar ratio is expected to decrease the catalyst degradation under photooxidative conditions. Interestingly, the degree of degradation of $H_2TPP(TCNE)_2$ may either decrease or increase at higher molar ratio of catalyst to cyclooctene. In other words, the cyclooctene concentration has a dual effect on the oxidation process. In one hand, the presence of higher amounts of the substrate reduces the possibility of direct oxidative attack of the reactive oxygen species (ROS) on the porphyrinic photosensitizer and on the other hand, allowing for more allylic hydroperoxide formation. The partial involvement of the allylic hydroperoxide in the oxidative degradation of the catalyst seems to be the cause of the unusually increased degradation of $H_2TPP(TCNE)_2$ at higher concentrations of cyclooctene.

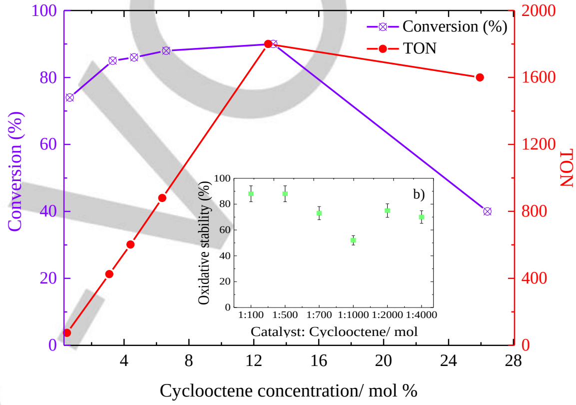


Figure 2. The optimization of the oxidation reactions using different molar ratios of $H_2TPP(TCNE)_2$:cyclooctene (1:X) in DCE upon irradiation with a 150 W metal halide lamp for 24 h. The photooxygenation reactions were performed using 6.6×10^{-4} mmol of the catalyst.

The reaction was performed using various LED lamps as the light source (Table 1). The blue LED lamps were much better than the red ones (Entries 1, 10 also 3, 12). Although the use of a 20 W blue LED lamp instead of a 10 W lamp light source had little effect on the rate of the oxidation reaction in DCE, major effects (lower conversion and oxidative stability) were observed in the case of toluene. However, depending on the used solvent, the increase in the lamp power may lead to a small or remarkable increase in photooxidation rate. It should be noted that these findings were similar to those observed in the oxidation of cyclooctene catalyzed by $H_2TPP(DDQ)_2$ (Entries 2, 6 also 11, 16). In contrast to that observed in the case of $H_2TPP(DDQ)_2$[18], for the reaction catalyzed by $H_2TPP(TCNE)_2$, acceptable conversions may be achieved using the red LED lamps as the light source (Entries 10, 11 also 13, 14 and 15, 16).

Solvent effects

Due to close dependence of the lifetime of singlet oxygen and the excited states of photosensitizers on the solvent properties[19], solvent plays crucial roles in photocatalytic processes. The oxidation of cyclooctene was performed in chlorinated and non-chlorinated solvents as well as a perfluorocarbon (perfluorodecalin) to clarify the solvent effects on the rate of the photooxidation reaction (Figure 3). Also, the results were compared with those in the presence of $H_2TPP(DDQ)_2$[18]. The optimized reaction times for the oxidation catalyzed by $H_2TPP(TCNE)_2$ and $H_2TPP(DDQ)_2$ were 24 and 72 h, respectively. However, the solvent effects were more pronounced for the reaction catalyzed by the former (Figure 3). Perfluorodecalin/Toluene and perfluorodecalin/DCE combinations were more efficient than the other solvents. However, there is no large difference between the conversions achieved in the mixed solvents in comparison with those in neat toluene or DCE. Furthermore, acetonitrile as a non-chlorinated solvent is a more convenient solvent from the green chemistry point of view[20]. Interestingly, the conversions obtained in acetonitrile were comparable with those obtained in the most efficient solvents of the series. Accordingly, the former may be used as an efficient alternative to the more expensive perfluorocarbons and toxic chlorinated solvents.

Table 1. The oxidation of cyclooctene in the presence of $H_2TPP(TCNE)_2$ (1:2) irradiated by LED lamps for 24 h.

Entry [Ref]	LED lamp	Solvent	Conversion [stability][a] (%)	Φ[b]	TON (TOF)[c] (h^{-1})
1	Blue (10 W)	DCE	89 [90]	0.32	890 (37.1)
2 [18]	Blue (10 W)	DCE	45 [87]	0.16	450 (18.8)
3	Blue (10 W)	Toluene	39 [63]	0.14	390 (16.3)
4	Blue (20 w)	Toluene	5 [27]	0.05	50 (2.1)
5	Blue (20 W)	DCE	89 [99]	0.53	890 (37.1)
6 [18]	Blue (20 W)	DCE	90 [15]	0.62	900 (37.5)
7[d,e]	Blue (20 W)	DCE	43 [0]	0.25	430 (17.9)
8	Blue (20 W)	CH_3CN[f]	10[g]	0.3	100 (4.2)
9 [18]	Blue (20 W)	CH_3CN[f,h]	-	-	-
10	Red (10 W)	DCE	58 [99]	0.17	580 (24.2)
11 [18]	Red (10 W)	DCE	10 [69]	0.03	100 (4.2)
12	Red (10 W)	Toluene	8 [83]	0.02	80 (3.3)
13	Red (20 W)	Toluene	18 [94]	0.03	180 (2.5)
14 [18]	Red (20 W)	Toluene	Trace	-	-
15	Red (20 W)	DCE	88 [98]	0.13	880 (12.2)
16 [18]	Red (20 W)	DCE	29 [91]	0.04	290 (4.0)

[a] The data in the bracket is the oxidative stability of the photosensitizer (%). [b] 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: For more details see the experimental section. [c] TOF was obtained as turnover number of the reaction per time unit. [d] The oxidation reaction was carried out in the presence of H_2TPP. [e] The reaction was carried out under basic condition of tetra-n-butylammonium hydroxide (0.5 ml). [f] The reaction was conducted at 0-5 ˚C. [g] The adduct was partially dissociated to H_2TPP and TCNE after 14 h and therefore the reaction was terminated. [h] The reaction was not studied due to the appreciable dissociation of the adduct to H_2TPP and DDQ under light exposure within 120 min of the beginning of the reaction.

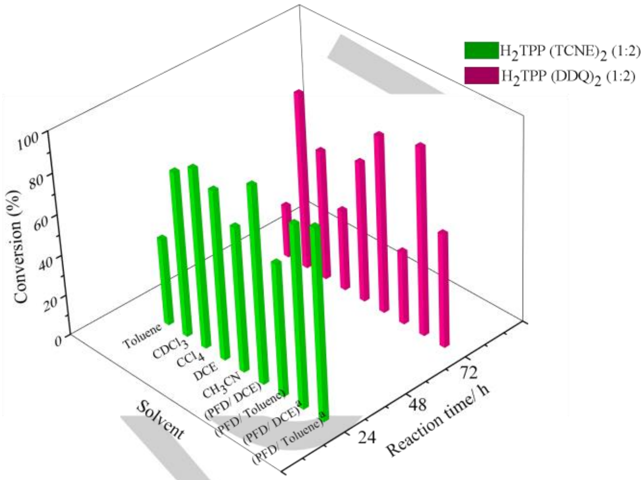


Figure 3. Solvent effects on the oxidation reactions of cyclooctene catalyzed by $H_2TPP(TCNE)_2$ and $H_2TPP(DDQ)_2$. The reaction mixture was irradiated by a 150 W metal halide lamp. [a] A 5-fold increase in the catalyst concentration was used in the oxidation reactions.

Substituents effects

The peripheral substituents of porphyrins have significant effects on the catalytic activity and oxidative stability of porphyrin-based catalyst and photocatalysts [21]. Also, the position of the absorption bands of porphyrins in UV-vis spectra is determined by the electronic and steric properties of the peripheral substituents. The presence of electron-donating substituents at the meso positions was found to shift the Soret and Q(0,0) bands to higher wavelengths that is more pronounced in the case of porphyrin dications and molecular complexes[6b, 6c]. These spectral changes influence the overlap between the emission bands of the light source and the absorption bands of the photosensitizer[18]. Moreover, the stability of porphyrinic catalysts towards oxidative degradation depends on the stereoelectronic properties of these substituents. The oxidation of cyclooctene was studied using the TCNE and DDQ molecular complexes of a series of electron-rich and electron-deficient meso-tetra(aryl)porphyrins in in acetonitrile (Figure 4). The stability of the TCNE adducts decreased in the order $H_2TPP(TCNE)_2 \geq H_2T(4\text{-ClP})P(TCNE)_2 \geq H_2T(4\text{-CH}_3P)P(TCNE)_2 >> H_2T(4\text{-OCH}_3P)P(TCNE)_2$. Also, the catalytic activity of the adducts on the basis of the conversion values decreased as $H_2T(4\text{-ClP})P(TCNE)_2 \geq H_2TPP(TCNE)_2 > H_2T(4\text{-CH}_3P)P(TCNE)_2 >> H_2T(4\text{-OCH}_3P)P(TCNE)_2$. It is observed that the catalytic activity of the molecular complexes correlates with the electron-deficiency of the porphyrins. However, no close correlation was observed between the order of the stability of the photosensitizers and the electronic effects of the meso groups. It should be noted that in this comparison, both the dissociation of molecular complexes and the oxidative degradation of the porphyrin photosensitizers were considered as the criteria of the catalyst stability. On the other hand, while the efficacy of the DDQ complexes was as $H_2T(4\text{-ClP})P(DDQ)_2 \approx H_2TPP(DDQ)_2 \geq H_2T(4\text{-CH}_3P)P(DDQ)_2 >> H_2T(4\text{-OCH}_3P)P(DDQ)_2$ their stability decreases as $H_2T(4\text{-ClP})P(DDQ)_2$ ≈ $H_2T(4\text{-CH}_3P(DDQ)_2$> $H_2TPP(DDQ)_2$ > $H_2T(4\text{-OCH}_3P)P(DDQ)_2$.

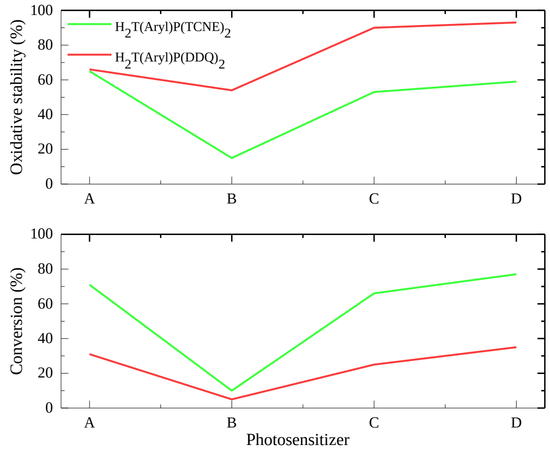


Figure 4. Substituent effects on the photocatalytic performance of TCNE and DDQ molecular complexes of A: H_2TPP, B: $H_2T(4\text{-OCH}_3P)P$, C: $H_2T(4\text{-CH}_3P)P$, D: $H_2T(4\text{-ClP})P$ in the oxidation reactions of cyclooctene upon irradiation with a 150 W metal halide lamp in acetonitrile at (0-5 °C).

The substituent effects on the catalytic efficiency of TCNE molecular complexes were also investigated in DCE (Table 2). When porphyrins and TCNE were used in 1:2 molar ratio, the photocatalytic activities decreased as $H_2T(4\text{-ClP})P(TCNE)_2$ ≈ $H_2T(4\text{-CH}_3P)P(TCNE)_2$ ≥ $H_2TPP(TCNE)_2$ > $H_2T(2\text{-CH}_3P)P(TCNE)_2$> $H_2T(4\text{-OCH}_3P)P(TCNE)_2$. It is observed that in the case of the former three complexes, the meso substituent has little effect on the catalytic activity of the photosensitizer. The decreased catalytic activity of $H_2T(2\text{-CH}_3P)P(TCNE)_2$ seems to be due to the steric hindrance of the ortho methyl groups. In other words, the presence of bulky methyl group prevents the formation of a tight molecular complex between the porphyrin and TCNE. Also, the decreased catalytic efficiency of $H_2T(4\text{-OCH}_3P)P(TCNE)_2$ may be attributed to the substantial photooxidative degradation of this molecular complex. The molecular complexes of the electron-deficient porphyrins (4-Clphenyl) and those with steric hindrance at the ortho position (2-methylphenyl) were exposed to partial decomposition upon dilution of the molecular complexes to the concentration required for the catalytic studies. Accordingly, the catalytic activity of the latter was studied at relatively low temperatures (0-5 °C). Also, TCNE was used in excess amounts beyond the 1:2 molar ratio to prevent the decomposition of the adducts to TCNE and the free base porphyrins. However, in the case of the other porphyrins, the comparison of the results (entries 1, 3, 4, 5, 6 and 7, Table 2) showed little improvements in the catalytic activity and oxidative stability of the molecular complexes caused by the excess TCNE. A literature survey[19, 22] shows that different factors such as the efficiency of singlet oxygen formation, lifetime of the singlet and triplet excited states, fluorescence quantum yield, intersystem crossing rate constant, degree of overlap between the emission and absorption bands of the light source and the photosensitizer as well as the oxidative stability of the catalyst may be considered to be involved in the catalytic performance of the porphyrin photosenisitizers. Accordingly, the observed order of catalytic activity and stability is not predictable on the basis of the known stereoelectronic properties of the meso substituents.

Table 2. Photooxidation of cyclooctene catalyzed by $H_2T(Aryl)P(TCNE)_2$ upon irradiation with a 150 W metal halide lamp in DCE for 24 h.

Entry	Photosensitizer	Conversion [Stability]^a(%)	TON (TOF) (h^{-1})
1	$H_2TPP(TCNE)_2$ (1:2)	83 [95]	830 (34.6)
2	$H_2TPP(TCNE)_2$ (1:2)	75 (0.88)^b	750 (31.3)
3	$H_2TPP(TCNE)_2$ (1:6)	87 [93]	870 (36.3)
4	$H_2T(4\text{-OCH}_3P)P(TCNE)_2$ (1:2)	23 [9]	230 (9.6)
5	$H_2T(4\text{-OCH}_3P)P(TCNE)_2$ (1:6)	28 [11]	280 (11.7)
6	$H_2T(4\text{-CH}_3P)P(TCNE)_2$ (1:2)^c	86 [95]	860 (17.9)
7	$H_2T(4\text{-CH}_3P)P(TCNE)_2$ (1:6)^c	86 [97]	860 (17.9)
8	$H_2T(4\text{-ClP})P(TCNE)_2$ (1:2)^{c,d}	89 [96]	890 (18.5)
9	$H_2T(2\text{-CH}_3P)P(TCNE)_2$ (1:10)^d	57 [10]	570 (23.8)

[a] The data in the bracket is the oxidative stability of the photosensitizer (%). [b] The reaction has been done in the presence of the cut-off filters (see ESI, S7). The data in the parenthesis is the quantum yield (Φ) of the reaction at λ_{max} = 436 nm. [C] 48 h. [d] The reaction was conducted at relatively low temperature (0-5 °C).

Oxidation of cyclohexene

The oxidation of cyclohexene catalyzed by the TCNE and DDQ molecular complexes and the free base porphyrins led to the formation of 2-cyclohexen-1-one as the sole product. The results for TCNE molecular complexes are summarized in Table 3. The catalytic activity and stability of the molecular complexes were as $H_2T(4\text{-ClP})P(TCNE)_2$ ≥ $H_2TPP(TCNE)_2$ ≈ $H_2T(4\text{-CH}_3P)P(TCNE)_2$ > $H_2T(4\text{-OCH}_3P)P(TCNE)_2$ >> $H_2T(2\text{-CH}_3P)P(TCNE)_2$ and $H_2T(4\text{-ClP})P(TCNE)_2$ ≥ $H_2TPP(TCNE)_2$ ≈ $H_2T(4\text{-CH}_3P)P(TCNE)_2$ >> $H_2T(4\text{-OCH}_3P)P(TCNE)_2$ ≈ $H_2T(2\text{-CH}_3P)P(TCNE)_2$, respectively. The observed orders are in agreement with those found in the oxidation of cyclooctene. Again, the reaction times were much shorter in the presence of the TCNE complexes in comparison with those in the presence of the DDQ ones. However, the difference between the catalytic activity of the TCNE and DDQ complexes is much more significant in the oxidation of cyclohexene. (Compare Figures 5 and 7. See also ESI S10 and S12).

Table 3. Photooxidation of cyclohexene catalyzed by $H_2T(Aryl)P(TCNE)_2$ upon irradiation with a 150 W metal halide lamp in DCE for 24 h.

Entry	Photosensitizer	Conversion [Stability]^a(%)	TON (TOF) (h^{-1})
1	$H_2TPP(TCNE)_2$ (1:2)	90 [92]	900 (37.5)
2	$H_2T(4\text{-}OCH_3P)P(TCNE)_2$ (1:2)	76 [7]	760 (31.7)
3	$H_2T(4\text{-}CH_3P)P(TCNE)_2$ (1:2)^b	89 [91]	890 (18.5)
4	$H_2T(4\text{-}ClP)P(TCNE)_2$ (1:2)^c	93 [93]	930 (38.8)
5	$H_2T(2\text{-}CH_3P)P(TCNE)_2$ (1:10)^c	15 [6]	150 (6.3)

[a] The data in the bracket is the oxidative stability of the photosensitizer (%). [b] 48 h. [c] The reaction was conducted at relatively low temperature (0-5 °C).

TCNE molecular complexes versus the DDQ ones and the free base porphyrins

The NMR and IR studies revealed that the cyano groups of TCNE and DDQ are involved in donor-acceptor interactions with porphyrins[6b, 6c]. However, the acceptor molecules are of different sizes and Lewis acidities and therefore different photostability and photocatalytic performance are expected for the two series of molecular complexes. The conducting of the oxidation of cyclooctene (Figures 5 and 6, ESI, S10 and S11) and cyclohexene (Figures 7 and 8, ESI, S12 and S13) in the presence of different photosensitizers revealed that the TCNE molecular complexes were much more efficient than the DDQ counterparts and the free base porphyrins. The yield of the product for the oxidation of cyclooctene catalyzed by H_2TPP, $H_2TPP(TCNE)_2$ and $H_2TPP(DDQ)_2$ in DCE are compared in Figure 5. The results showed higher performance of $H_2TPP(TCNE)_2$ relative to that of the free base porphyrin and the DDQ adduct. Also, that the maximum conversion of cyclooctene (83 %) was achieved at a much shorter reaction time (24 h) in the case of $H_2TPP(TCNE)_2$. It is noteworthy that a reaction time of 72 h was needed for achieving the maximum conversion in the presence of H_2TPP (33 %) and $H_2TPP(DDQ)_2$ (64 %). Also, the oxidative stability of the photosensitizers was compared (Figure 6 and ESI, S11).

The molecular complexes showed high stability than the free base porphyrins. In spite of the same oxidative stability of the molecular complexes in a time interval of 24 h, the DDQ complex was more stable at longer reaction times (Figure 6). It is noteworthy that the optimum catalyst to olefin molar ratios were 1:2000 and 1:1000, for the reaction catalyzed by the TCNE and DDQ molecular complexes, respectively. However, for the ease of comparison of the catalytic efficiency of the TCNE and DDQ molecular complexes and the free base porphyrins, all reactions were performed using the 1:1000 molar ratio.

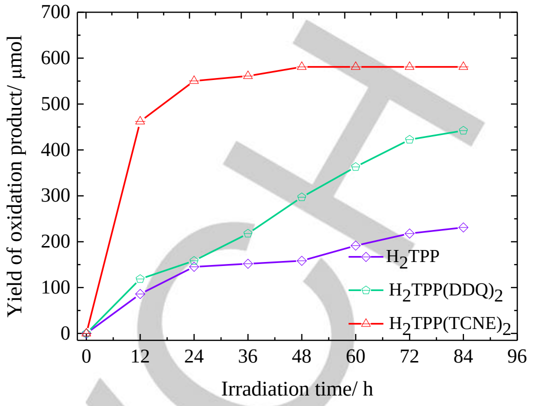


Figure 5. The rate of the oxidation reaction of cyclooctene photosensitized by H_2TPP, $H_2TPP(DDQ)_2$ and $H_2TPP(TCNE)_2$.

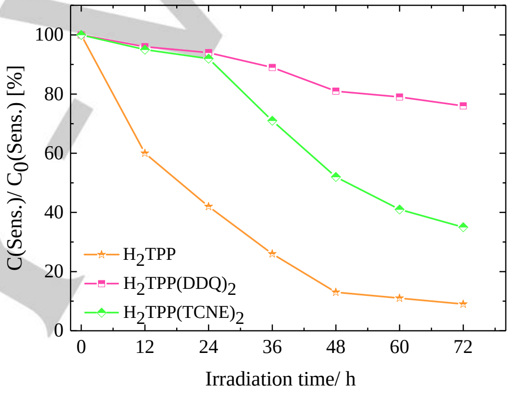


Figure 6. The photooxidative stability of H_2TPP, $H_2TPP(DDQ)_2$, $H_2TPP(TCNE)_2$ under the oxidation reaction of cyclooctene.

The photocatalytic activity of the three photosensitizers was also compared in the oxidation of cyclohexene (Figure 7). Herein, the catalytic activity of the TCNE complex was significantly higher than that of the DDQ complex and H_2TPP. Again, the molecular complexes have higher photostabilities than the free base porphyrin. Interestingly, the TCNE adduct is more stable than the DDQ molecular complex (Figure 8).

In a previous study, we have found that the oxidation of olefins with the DDQ complexes and the free base porphyrins proceeds mainly via a singlet oxygen mechanism[18]. The singlet oxygen quantum yield (φ_Δ) of the photosensitizers has been used as a criterion to evaluate the relative efficacy of different photocatalysts. The singlet oxygen quantum yield of the free base porphyrins and the molecular complexes determined relative to that of methylene blue ($\varphi_\Delta = 0.57$) using DPBF as the singlet oxygen quencher[23] are summarized in Table 4.

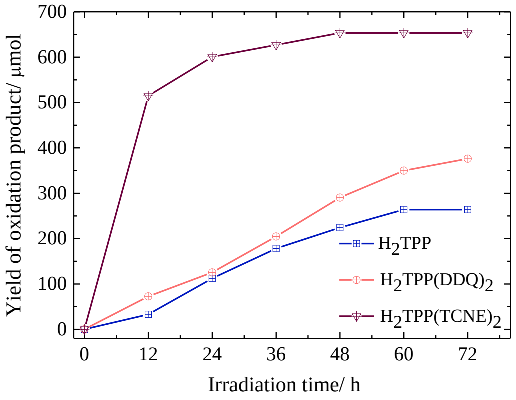


Figure 7. The rate of the oxidation reaction of cyclohexene photosensitized by H_2TPP, $H_2TPP(DDQ)_2$ and $H_2TPP(TCNE)_2$.

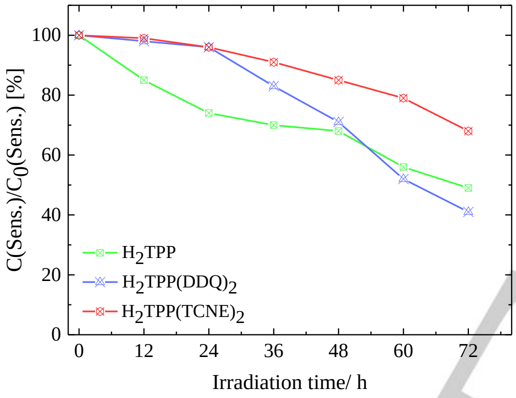


Figure 8. The photooxidative stability of H_2TPP, $H_2TPP(DDQ)_2$ and $H_2TPP(TCNE)_2$ under the oxidation reaction of cyclohexene.

The significantly higher $φ_Δ$ values of the TCNE complexes ($φ_Δ$= 0.57-0.98) with respect to that of the DDQ molecular complexes ($φ_Δ$= 0.03-0.57) and the free base porphyrins (0.32-0.63) may explain the higher efficiency of the former (Figure 9 and ESI, S8). It is noteworthy that both the photostability and $φ_Δ$ values of the photosensitizers are involved in the observed order of catalytic performance of different molecular complexes and free base porphyrins. However, the significantly higher catalytic activity of the TCNE complexes correlates well with their remarkably higher $φ_Δ$ values.

Table 4. Singlet oxygen quantum yield of $H_2T(Aryl)P$, $H_2T(Aryl)P(DDQ)_2$ and $H_2T(Aryl)P(TCNE)_2$ determined using DPBF as singlet oxygen quencher [a].

Entry	Photosensitizer	$Φ_Δ$
1	H_2TPP	0.63
2	$H_2TPP(DDQ)_2$	0.03
3	$H_2TPP(TCNE)_2$	0.80
4	$H_2T(4\text{-}OCH_3P)P$	0.32
5	$H_2T(4\text{-}OCH_3P)P(DDQ)_2$	0.16
6	$H_2T(4\text{-}OCH_3P)P(TCNE)_2$	0.98
7	$H_2T(4\text{-}CH_3P)P$	0.47
8	$H_2T(4\text{-}CH_3P)P(DDQ)_2$	0.17
9	$H_2T(4\text{-}CH_3P)P(TCNE)_2$	0.57
10	$H_2T(4\text{-}ClP)P$	0.36
11	$H_2T(4\text{-}ClP)P(DDQ)_2$	0.57
12	$H_2T(4\text{-}ClP)P(TCNE)_2$	0.57
13	$H_2T(2\text{-}CH_3P)P$	0.45
14	$H_2T(2\text{-}CH_3P)P(DDQ)_2$	-[b]
15	$H_2T(2\text{-}CH_3P)P(TCNE)_2$	-[b]

[a] Singlet oxygen quantum yield of different photosensitizers was determined using methylene blue as standard upon irradiation with a 10 W red LED lamp. The kinetic curves used for the evaluation of $φ_Δ$ are summarized in ESI, S8. [b] Due to the partial decomposition of the molecular complexes to $H_2T(2\text{-}CH_3P)P$ and the corresponding Lewis acid at room temperature, the $φ_Δ$ values were not evaluated

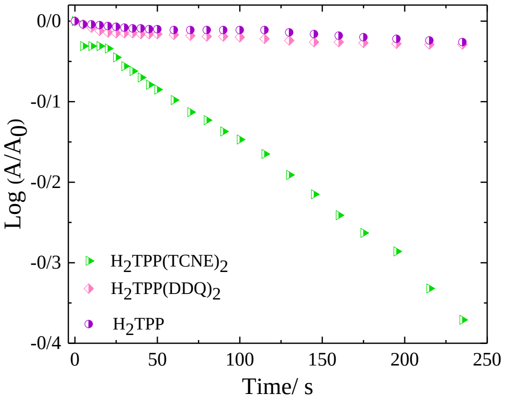


Figure 9. The rate of DPBF photooxidation catalyzed by H_2TPP, $H_2TPP(DDQ)_2$ and $H_2TPP(TCNE)_2$ upon irradiation with a 10 W red LED lamp.

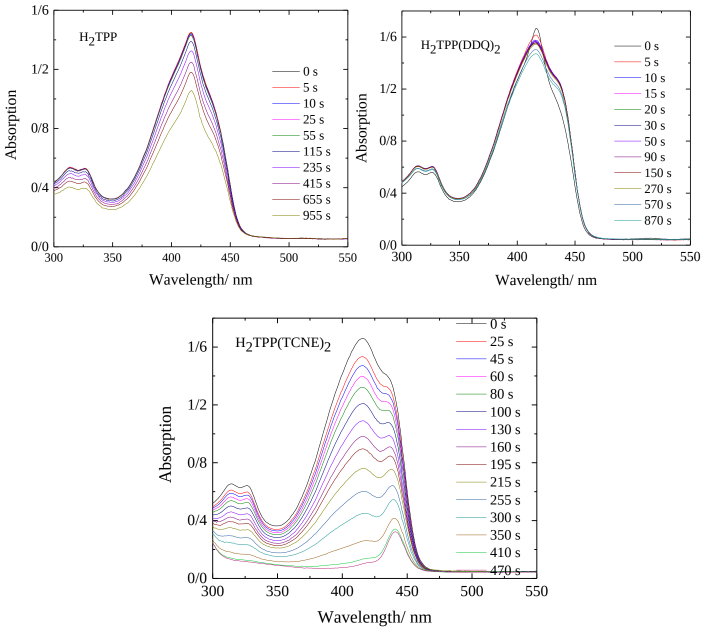


Figure 10. The changes in the absorption spectrum of DPBF under the reaction conditions catalyzed by H_2TPP, $H_2TPP(DDQ)_2$ and $H_2TPP(TCNE)_2$.

Proposed mechanism

The aerobic photooxidation of olefins in the presence of porphyrin photosensitizers may proceed through Type I and type II mechanisms with the involvement of superoxide anion radical and singlet oxygen species as ROS, respectively[24]. Recently, the oxidation of olefins with molecular oxygen catalyzed by $H_2TPP(DDQ)_2$ was found to occur predominantly through a type II mechanism[18]. The fluorescence emission changes at 484 nm (Figure 11) upon the addition of 1,3-diphenylisobenzofuran (DPBF) to a DCE solution of $H_2TPP(TCNE)_2$ was in accord with the formation of singlet oxygen upon the excitation of the porphyrin photosensitizer[25]. It should be noted that DPBF as the singlet oxygen quencher readily and exclusively reacts with this species. Also, no detectable change was observed in the rate of the photooxidation of cyclooctene due to the addition of 1,4-benzoquinone as the scavenger of superoxide anion radical. Accordingly, as was evident in the case of $H_2TPP(DDQ)_2$[18], a singlet oxygen mechanism is mainly involved in the oxidation reaction (Scheme 1).

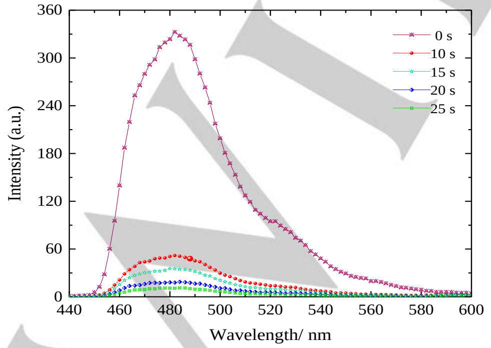
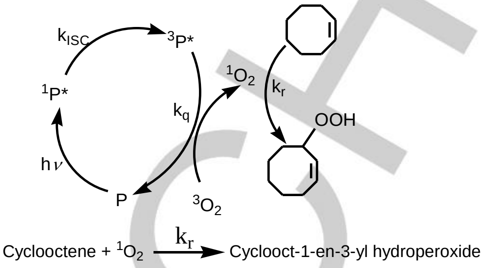


Figure 11. The fluorescence emission spectral changes of DPBF at 484 nm under the reaction conditions catalyzed by $H_2TPP(TCNE)_2$.



$$\text{Cyclooctene} + {}^1O_2 \xrightarrow{k_r} \text{Cyclooct-1-en-3-yl hydroperoxide}$$

k_{ISC} and k_q, show the intersystem crossing and quenching rate constants, respectively. P = photosensitizer.

Scheme 1. Proposed mechanism.

Conclusion

The TCNE and DDQ molecular complexes of a series of electron-deficient and electron–rich porphyrins were used as more stable and red-shifted porphyrinic photosensitizer for the aerobic oxidation of cyclooctene and cyclohexene under mild conditions. The significantly increased photocatalytic activity observed for the TCNE molecular complexes with respect to that of the free base porphyrins showed that the porphyrin photosensitizers may be modified by core substitution of porphyrins with Lewis acids. It is noteworthy that the higher catalytic activity of the former was achieved in the much shorter reaction time. On the other hand, the remarkably higher catalytic performance of the TCNE molecular complexes than the corresponding DDQ ones demonstrates the crucial role played by the nature of acceptor molecule in the extent of modification of the porphyrin photosensitizer. The singlet oxygen quantum yields of the former were much higher than those of the latter and the free base porphyrins which may explain the preference of the TCNE complexes over the DDQ ones and the free base porphyrins. However, more experimental and theoretical studies are in progress to elucidate the effects of acceptor molecules on the excited states properties of porphyrins. Also, due to the lack of X-ray crystallographic information on the molecular complexes of TCNE and DDQ, computational studies should be performed to reveal the structural difference between the two series of molecular complexes.

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 (phenylmethylsiloxane 30 m × 320 µm × 0.25 µm) and a flame-ionization detector was utilized in GC analyses.

Synthesis and characterization

The free base porphyrins including $H_2T(4\text{-}X)PP$ (X= H, OCH_3, CH_3, Cl) and $H_2T(2\text{-}X)PP$ (X= CH_3, Cl) were prepared and characterized according to the literature methods[26]. The ^1H NMR, ^{13}C NMR and UV-Vis spectral data of the porphyrins are presented in the ESI, S1.

Preparation of the DDQ and TCNE molecular complexes

$H_2T(4\text{-}X)PP(DDQ)_2$ and $H_2T(4\text{-}X)PP(TCNE)_2$ were prepared using the procedure reported by Mohajer et al[6b, 6c]. The free base porphyrins with DDQ and or TCNE were added to CH_2Cl_2 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 the reaction. Slow evaporation of CH_2Cl_2 at room temperature gave a dark green solid that was characterized by UV-vis, ^1H and ^{13}C NMR spectroscopy (ESI, Figure S2, S3 and S4). In the case of $H_2T(2\text{-}CH_3P)P(DDQ)_2$ and $H_2T(2\text{-}CH_3P)P(TCNE)_2$ due to decreased basicity of the porphyrins[27] and the steric effects of meso-aryl substituents, excess amounts of DDQ or TCNE (1:10- 1:15 molar ratio) were needed to shift the equilibrium towards the molecular complexes. The dichloromethane solution was stirred for ca. 10 days. The dark green solids obtained by slow evaporation of the solvent were characterized by UV-vis, ^1H and ^{13}C NMR spectroscopy (ESI, Figure S2, S3, S4). The DDQ and TCNE molecular complexes of $H_2T(2\text{-}ClP)P$ as the weakest base of the series[27], were substantially decomposed to $H_2T(2\text{-}ClP)P$ and the corresponding Lewis acid at the concentrations used for the photooxidation reactions and therefore no further studies was conducted on the molecular complexes of $H_2T(2\text{-}ClP)P$.

General oxidation procedure

A double walled cylindrical glass vessel equipped with water circulation (ESI, S5) was used as the reactor. The details of photooxidation reactions and chemical actinometry measurements are presented in ESI, S6 and S7.

Singlet oxygen quantum yield measurement

The quantum yield of singlet oxygen formation of the photosensitizers was measured by using 1,3-diphenylisobenzofuran (DPBF) as the quencher of singlet oxygen and methylene blue ($\varphi_\Delta = 0.57$ in dichloromethane) as a reference photosensitizer[28]. The equation proposed by Murata et al.[29], $\Phi_\Delta = \Phi_\Delta^{std}(\upsilon_i \times I^{std} / \upsilon_i^{std} \times I)$ was used to evaluate the φ_Δ values. In a control reaction it was found that exposure of the dichloromethane solution of DPBF (8.0×10^{-4} M) to the 10 W red LED lamp led to no detectable degradation of DPBF (ESI, S8). The Kinetics curves used for the φ_Δ measurements and the changes in the absorption spectrum of DPBF in the presence of different photosensitizers are shown in ESI, S8 and S9.

Acknowledgements

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Keywords: Photooxidation • Porphyrins • Donor-acceptor molecular complexes • Tetra-cyanoethylene • 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

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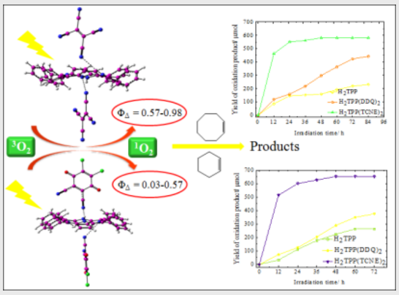
FULL PAPER

Significantly enhanced photocatalytic activity, photostability and singlet oxygen quantum yield of the TCNE molecular complexes of meso-tetra(aryl)porphyrins relative to those of the free base porphyrins are reported



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