



Photocatalytic behaviour of tantalum (V) phthalocyanines in the presence of gold nanoparticles towards the oxidation of cyclohexene

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ABSTRACT

This paper presents the photocatalytic oxidation of cyclohexene using $(\text{OH})_3\text{TaPc}$ derivatives in the absence or presence of gold nanoparticles (AuNPs). The photochemical parameters that include photodegradation (Φ_P) and singlet oxygen (Φ_Δ) quantum yields are also reported in this work. The Φ_Δ values were 0.47 and 0.36 for complexes **1a** and **1b**, respectively. The Φ_Δ values improved drastically in the presence of AuNPs to 0.75 and 0.88, respectively. The Φ_P values ranged from 1.02 to 2.45×10^{-6} , showing stability of TaPc derivatives in the absence and presence of AuNPs. The photocatalytic products identified using gas chromatograph (GC) are cyclohexene oxide, 2-cyclohexen-1-ol, 2-cyclohexene-1-one and 1,2-cyclohexanediol. The percentage conversion values were higher in the presence of AuNPs. Singlet oxygen was determined to be the main agent involved in the photocatalytic oxidation of cyclohexene. The product yield percentage values for both TaPc complexes (**1a** and **1b**) and TaPc in the presence of AuNPs ranged from 6.3 to 21.2%.

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1. Introduction

The oxidation of alkanes and alkenes has been studied extensively due to the usefulness of the oxidation products which are obtained. These include alcohols, ketones and aldehydes. These products are of great importance to industrial processes as well as fine chemical syntheses [1]. The oxidation of alkenes using phthalocyanines and a variety of oxidants has been reported before [2–8]. Photocatalytic oxidation is more favorable over the chemical (using oxidants) methods due to minimal environmental impact, the use of light as a renewable source of energy and use of milder conditions for the reactions in the former [2]. Phthalocyanines have been employed to photo-oxidize cyclohexene [3,9,10]. Xue et al. [10] employed palladium phthalocyaninesulfonate to selectively photo-oxidize cyclohexene. However, the photo-oxidation of alkenes using phthalocyanines is still limited compared to the oxidation of phenols [11,12].

Gold nanoparticles (AuNPs) have gained a lot of attention in the past decade due to their tunable optical properties that depend on size and shape [13]. AuNPs strongly absorb visible light due to the

surface plasmon resonance (SPR) effects [14]. The SPR effect is a collective oscillation of conduction electrons in the nano-particles, which resonate with the electromagnetic field of the incident light [15]. To the best of our knowledge, the photo-oxidation of alkanes or alkenes by phthalocyanines in the presence of AuNPs has not been studied. We therefore explore the photocatalytic oxidation of cyclohexene using $(\text{OH})_3\text{TaPc}$ (Fig. 1) complexes in the presence and absence of AuNPs. Ta as central metal was chosen due to the possibility of high singlet oxygen quantum yield induced by its large size. The photostability of the MPC complexes is important for their application as photocatalysts (photosensitizers), and their photostability in the presence of nanoparticles will be explored in this manuscript.

2. Experimental

2.1. Materials

Zinc(II) phthalocyanine (ZnPc), 1,3-diphenylisobenzofuran (DPBF), cyclohexene, cyclohexene oxide, 2-cyclohexene-1-ol, cyclohexene-1-one, 1,2-cyclohexanediol, 1,4-diazobicyclo-octane (DABCO), benzoquinone, toluene, sodium borohydride (NaBH_4), tetraoctylammonium bromide (TOABr) and gold (III) chloride were purchased from Aldrich. The syntheses of complexes **1a** and **1b** have been reported elsewhere [16].

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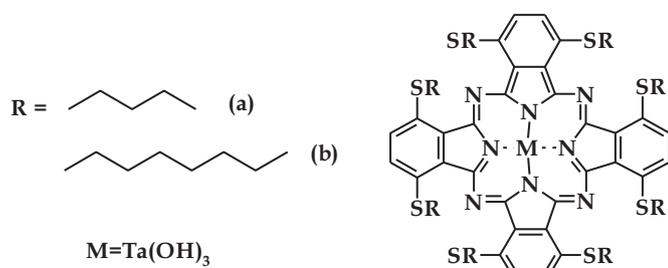


Fig. 1. Molecular structures of TaPc complexes (**1a** and **1b**).

2.2. Equipment

A Shimadzu UV - 2550 spectrophotometer was employed for the collection of UV–vis spectra. Transmission electron microscope (TEM) images were obtained using a JEOL JEM 1210 transmission electron microscope at 100 kV accelerating voltage.

Atomic force microscopy (AFM) images were recorded in the non-contact mode in air with a CP-11 Scanning Probe Microscope from Veeco Instruments (Carl Zeiss, South Africa) at a scan rate of 1 Hz. The images were obtained using a spring constant range of 20–80 N/m, and resonant frequency range of 217–276 Hz. Samples for AFM were prepared by spin coating solutions of AuNPs in toluene in the presence and absence of TaPc derivatives.

X-ray powder diffraction patterns were recorded on a Bruker D8, Discover equipped with a proportional counter, using Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$, nickel filter). Data were collected in the range from $2\theta = 5^\circ$ to 60° , scanning at 1° min^{-1} with a filter time-constant of 2.5 s per step and a slit width of 6.0 mm. Samples were placed on a silicon wafer slide. The X-ray diffraction data were treated using Eva (evaluation curve fitting) software. Baseline correction was performed on each diffraction.

2.3. Photochemical methods

General Electric Quartz line lamp (300 W) was employed for the determination of photodegradation and singlet oxygen quantum yields, and for the phototransformation of cyclohexene. A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations respectively. An interference filter (Intor, 740 nm with a band width of 40 nm) was additionally placed in the light path before the sample, hence ensuring excitation at the Q band only (700–780 nm). Experiments were also performed where white light (from quartz line lamp) or sunlight was employed. The wavelength range for unfiltered light is $\sim 400 \text{ nm}$ to near infrared region, hence it does not include the B band of phthalocyanines, but covers a wider absorption region. The unfiltered light will be referred to as white light in this work. Light intensities were measured with a POWER MAX 5100 (Molelectron detector incorporated) power meter.

The products for the phototransformation of cyclohexene were analysed using an Agilent HP 5890 gas chromatograph (GC), fitted with a flame ionization detector (FID), using a DB-5MS column (0.25 m length, 0.2 mm internal diameter, 0.25 μm film thickness). The GC parameters were as follows: the initial oven temperature was at 50°C , maximum oven temperature was 280°C , equilibration time was 0.15 min, initial ramp rate was $10^\circ\text{C}/\text{min}$ at 180°C for 2 min, the second was $10^\circ\text{C}/\text{min}$ at 280°C for 2 min and total run time was 27 min.

Reactions were carried out under homogeneous condition in toluene. The reaction mixture consisted of complexes **1a**, **1b** or **1a**-AuNP or **1b**-AuNP mixed with known concentration of the cyclohexene. The reaction mixture was contained in a reaction vessel maintained at room temperature under constant stirring, and

photolysed using the set-up described above. The reaction was then monitored by taking samples of the solution and recording UV spectra or gas chromatographs.

Light intensity for these studies were 14×10^{15} and 8×10^{16} photons $\text{s}^{-1} \text{ cm}^{-2}$ for filtered and white light, respectively.

2.4. Photochemical parameters

2.4.1. Singlet oxygen quantum yields

Quantum yields of singlet oxygen photogeneration by TaPc derivatives in toluene were determined in air (no oxygen bubbled) using the relative method with ZnPc as reference and DPBF as chemical quencher for singlet oxygen, using Eq. (1):

$$\Phi_{\Delta} = \Phi_{\Delta}^{\text{Std}} \frac{R_{\text{DPBF}}^{\text{Std}} I_{\text{abs}}^{\text{Std}}}{R_{\text{DPBF}}^{\text{Std}} I_{\text{abs}}} \quad (1)$$

where $\Phi_{\Delta}^{\text{Std}}$ is the singlet oxygen quantum yield for the standard, ZnPc ($\Phi_{\Delta} = 0.58$ in toluene [17]), R_{DPBF} and $R_{\text{DPBF}}^{\text{Std}}$ are the DPBF photodegradation rates in the presence of a sensitizer under investigation and the standard respectively. I_{abs} and $I_{\text{abs}}^{\text{Std}}$ are the rates of light absorption by the sensitizer and standard, respectively.

To avoid chain reactions induced by DPBF in the presence of singlet oxygen [18], the concentration of DPBF was lowered to $\sim 3 \times 10^{-5} \text{ mol dm}^{-3}$. Solutions of sensitizer (absorbance = 0.2 at the irradiation wavelength) containing DPBF were prepared in the dark and irradiated in the Q band region using the setup described above. DPBF degradation at 415 nm was monitored. The light intensity for singlet oxygen studies was 5×10^{15} photons $\text{s}^{-1} \text{ cm}^{-2}$ for filtered light (Q band irradiation). The light intensity for the white light was 2×10^{16} photons $\text{s}^{-1} \text{ cm}^{-2}$.

2.4.2. Photodegradation quantum yields

For determination of photodegradation quantum yields of the TaPc derivatives, the usual Eq. (2) [18] was employed for both Q band and white light irradiation:

$$\Phi_{\text{P}} = \frac{(C_0 - C_t) V N_A}{I_{\text{abs}} S t} \quad (2)$$

where C_0 and C_t (mol dm^{-3}) are the TaPc complex (**1a** and **1b**) concentrations before and after irradiation respectively; V is the reaction volume; S , the irradiated cell area (2.0 cm^2); t , the irradiation time (s); N_A , the Avogadro's number and I_{abs} , the overlap integral of the radiation source intensity and the absorption of the Pc (the action spectrum) in the region of the interference filter transmittance. For experiments where the TaPc complexes were irradiated in the presence of AuNPs, any absorption of the latter was subtracted from the DPBF absorption to avoid any errors.

2.5. Synthesis of gold nanoparticles (AuNPs)

The synthesis of gold nanoparticles (using phase transfer agent TOABr as a protecting ligand) was achieved following the method described by Brust et al. [19] and Kotiaho et al. [20] with slight modifications. Briefly gold (III) chloride trihydrate solution (25 mmol L^{-1} , 4 mL) was vigorously stirred with a solution of TOABr (85 mmol L^{-1} , 6 mL) in toluene until all the gold chloride was transferred to the organic phase, as judged by the change of colour from orange to red [19,20]. An aqueous solution of a reducing agent NaBH_4 ($3.6 \times 10^{-2} \text{ mol L}^{-1}$) was then added drop-wise over a period of 10 min. The mixture was then stirred vigorously for 30 min. The organic phase was separated and washed with water. The AuNPs were then characterized with transmission electron microscopy (TEM), atomic force microscopy (AFM) and X-ray diffraction (XRD). Solid complexes of conjugates of **1a** and **1b** with AuNPs were synthesized by mixing the two, allowing

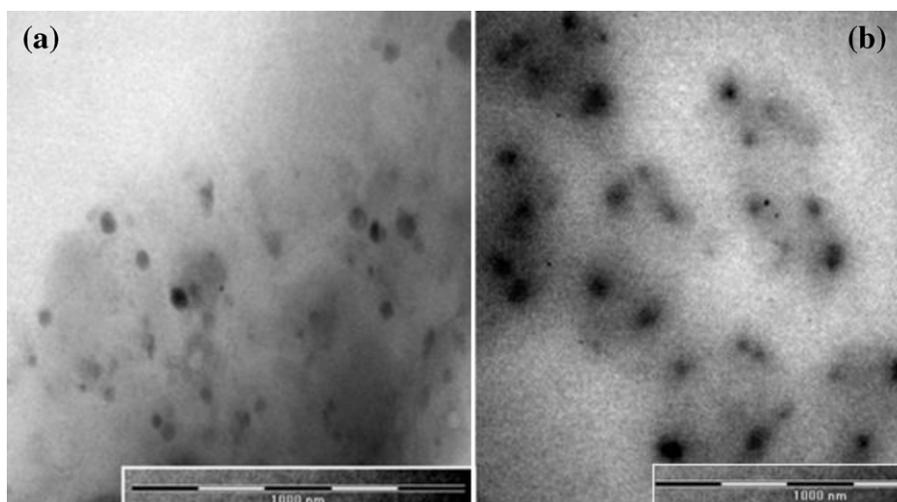


Fig. 2. TEM images of (a) AuNPs in water (b) AuNPs modified with complex 1a.

time (~28–30 h) for the MPcs to react with the gold nanoparticles. The solvent (toluene) was then evaporated. The uncoordinated TaPc derivatives were removed in a size-exclusion column (bio-beads).

3. Results and discussion

3.1. Characterization of AuNPs and AuNPs–MPc conjugates

Fig. 2 shows the TEM images of AuNPs (Fig. 2a) and MPc–AuNPs (Fig. 2b). Fig. 2a illustrates the distribution of the gold nanoparticles synthesized in this work. In Fig. 2b, the MPc appear to be ‘surrounding’ the gold nanoparticles. This is illustrated by the ‘shades’ around the dark spots.

The AuNPs were stabilized by TOABr; it is possible for the stabilizer to be replaced by the alkylthio groups of TaPc derivatives to form a bond, or that the TaPc derivatives are just adsorbed onto the AuNPs.

X-ray diffraction (XRD) provided important details about the crystal structure and properties of the AuNPs employed in this work. This technique was employed to determine the size of the particles using the Debye–Scherrer Eq. (3) [21]:

$$d(\text{Å}) = \frac{k\lambda}{\beta \cos \theta} \quad (3)$$

where k is an empirical constant equal to 0.9, λ is the wavelength of the X-ray source, (1.5405 Å), β is the full width at half maximum of the diffraction peak, and θ is the angular position of the peak. Fig. 3 shows the XRD pattern for the AuNPs employed in this work, with the peaks observed at 2θ values of 27.41°, 31.65°, 38.17°, 45.40° and 56.38°. The average size for the AuNPs was then worked out to be 10.1 nm, using the peak that fits the structure database reflection for gold.

Atomic force microscopy data (Fig. 4) provided the information about the morphology of AuNPs on a cross section of the glass surface coating from toluene in the absence and presence of the

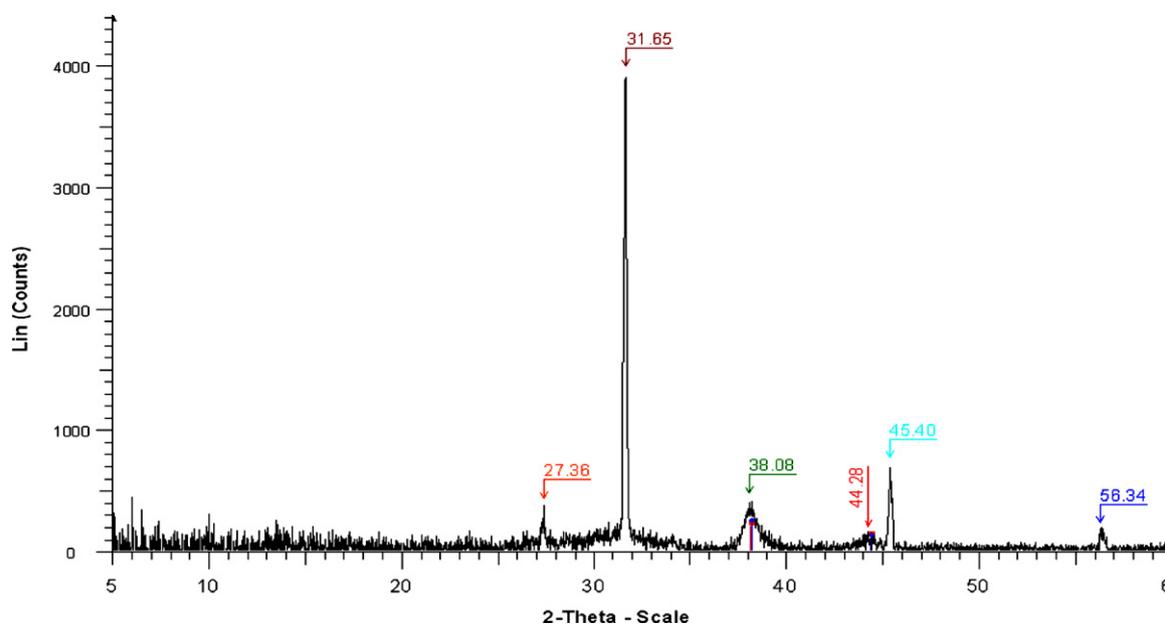


Fig. 3. X-ray diffractogram of AuNPs.

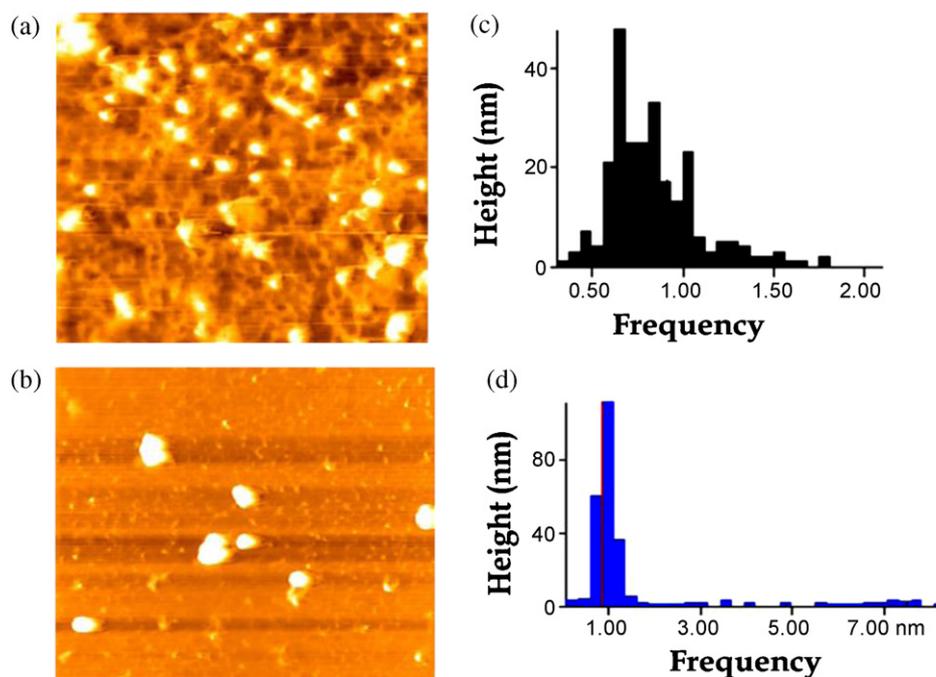


Fig. 4. AFM images of AuNPs in the absence (a) and presence (b) of complex **1a** deposited on a glass surface from toluene. The corresponding histograms are shown in (c) and (d).

TaPc derivatives. The average roughness (R_a) value of 0.628 nm was obtained for AuNPs alone and the value decreased to 0.0927 nm for AuNP-MPc conjugates. The decrease may be due to aggregation in the presence of TaPc derivatives.

The histogram in Fig. 4c, shows populations of AuNPs with size distributions from 20 nm and below in the section analysed, to occur more frequently. In Fig. 4d for AuNPs in the presence of complex **1a** there is domination by the larger sizes, with size distribution of up to 114 nm, showing increased aggregation. This indicates that modification of AuNPs with complexes **1a** and **1b** was successful to some extent.

3.2. Singlet oxygen quantum yield (Φ_{Δ}) of the TaPc derivatives

Singlet oxygen plays an important role in photocatalytic oxidation reactions [18]. Singlet oxygen quantum yield (Φ_{Δ}) values (Table 1) were determined using DPBF as the singlet oxygen quencher in toluene upon irradiation in the Q band region. The singlet oxygen quantum yield values determined under Q band irradiation were 0.47 and 0.36 in toluene for complexes **1a** and **1b**, respectively. In the presence of AuNPs, the Φ_{Δ} values of the TaPc complexes (**1a** and **1b**) increased significantly, almost doubling these values, due to the heavy atom effect of the gold nanoparticles. The AuNPs promote a higher production of singlet oxygen due to enhanced triplet excited state yield of the sensitizer. Improved singlet oxygen generation by metal nanoparticles has been observed and reported by Zhang et al. [22]. Silver nanoparticles were employed by Zhang et al. [22], and the photosensitizer was described as being 'sandwiched' in between the silver nanoparticle island films enabling more singlet oxygen production due to enhanced triplet excited yield of the sensitizer. Their concept may be related to this study where gold nanoparticles are employed instead of silver nanoparticles. In addition, it is possible that the presence of the bromide atoms on the TOABr (the AuNPs protecting ligand) increases the energy transfer to the triplet state of TaPc complexes in the presence of AuNPs, through enhanced spin-orbit coupling as a result of the heavy atom effect [23].

3.3. Photodegradation quantum yields (Φ_P) of the TaPc derivatives

3.3.1. Q band irradiation

Photostability of MPc complexes is important for their application as photocatalysts (photosensitizers). Photodegradation is a photochemical process whereby the conjugated chromophore of the phthalocyanine ring gets degraded into smaller molecular fragments. This process is driven by singlet oxygen in the presence of visible light to afford the photo-oxidation product, phthalimide, as suggested by Shcnurpfeil et al. [18]. The photodegradation stabilities were determined in toluene by monitoring the spectra of the complexes with increasing time, during photolysis, Fig. 5a. The MPc complexes are degraded by singlet oxygen generated by them. Several factors can influence Φ_P , such as the nature of the solvent and the substituents on the phthalocyanine ring. In general the TaPc complexes were very stable, the Φ_P values ranged from 1.02 to 2.45×10^{-6} . Typical values for unstable phthalocyanines are of the order of 10^{-3} [24]. Generally, complex **1b** is more stable than **1a** in the absence and presence of AuNPs.

The mechanism (Type II) [25] for degradation of phthalocyanines under visible light is as outlined in Scheme 1, which shows that the degradation of MPc complexes is mediated by singlet oxygen [25].

The photodegradation of TaPc derivatives followed first order kinetics with the plots of $\ln(C_0/C)$ (where C and C_0 are absorbances measured for the Q band of the MPc complex at time t and t_0 , respectively) versus time in seconds, shown in Fig. 6(iii and iv). The slopes of the plots gave the effective reaction rate constants, k . Table 1 shows a decrease in rate constants for degradation of complexes **1a** and **1b** in the presence of AuNPs.

3.3.2. White light irradiation

The photostability of the MPc complexes depends mainly on the type of radiation. These complexes are more stable in visible light compared to UV irradiation [26]. Irradiation using white light will include the Q band, but it is more extended than the Q band irra-

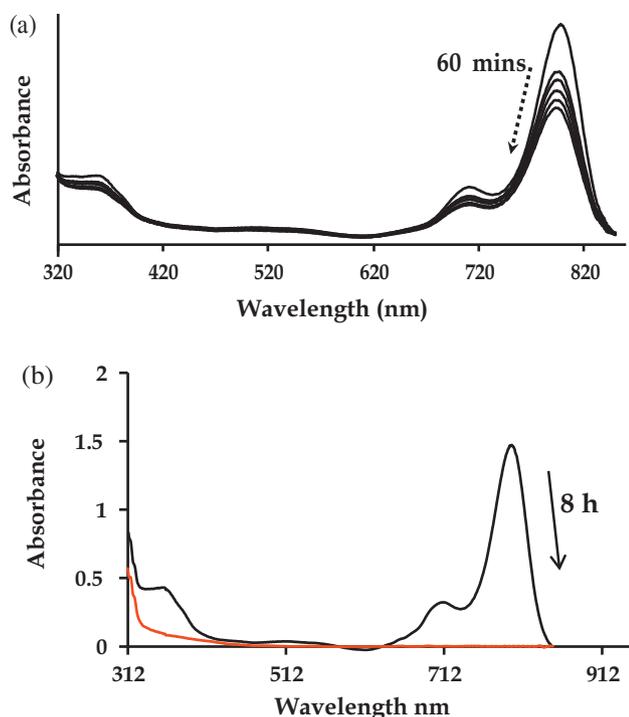


Fig. 5. Photodegradation spectra of complex **1a** in toluene by (a) Q band irradiation. $[1a] = 2.3 \times 10^{-5} \text{ mol L}^{-1}$ and (b) direct sunlight. Concentration: $[1a] = 3.1 \times 10^{-5} \text{ mol L}^{-1}$. Irradiation over a period of 8 h min.



Scheme 1. Type II mechanism. Here MPc is the metallophthalocyanine, ISC is intersystem crossing and Subs is the substrate. ^3O_2 represents $\text{O}_2(^3\Sigma_g)$ and ^1O_2 represents $\text{O}_2(^1\Delta_g)$.

diation (which ranges from 700 to 780 nm for the TaPc derivatives under discussion).

The TaPc complexes (**1a** and **1b**) were completely degraded by exposure to sunlight (for 8 h), Fig. 5b, whose main intensity is at $\sim 550 \text{ nm}$. In order to study the degradation of the complexes under more controlled conditions, we employed white light from a tungsten lamp (400–900 nm), to photodegrade the complexes in the presence and absence of AuNPs.

In the presence of AuNPs, irradiation of both TaPc derivatives and the AuNPs is possible, complicating the spectra. At the wavelength of the tungsten lamp, it is not expected that the excitation will be at the B band of the phthalocyanine molecule, however, there will be a larger wavelength range as opposed to the excitation of the Q band only. Thus singlet oxygen by Scheme 1 is expected

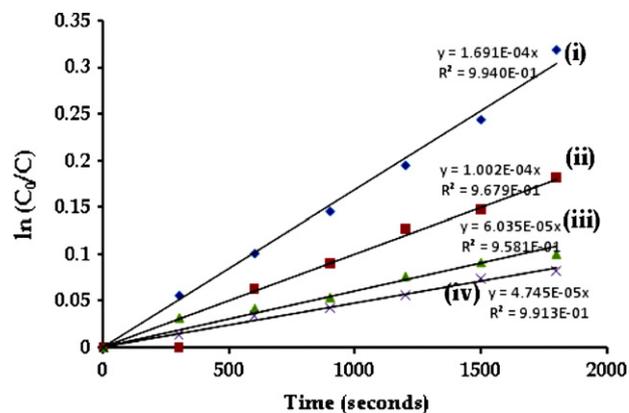


Fig. 6. A plot of $\ln(C_0/C)$ vs. time for conjugates under white irradiation: **1b**-AuNPs (i) and **1a**-AuNPs (ii) and under Q band irradiation: **1a**-AuNPs (iii) and **1b**-AuNPs (iv). Solvent = toluene.

to be the dominant route for degradation under white light from the tungsten lamp.

Photolysis induced by UV irradiation of the MPC derivatives has been shown to follow first-order kinetics [27]. Plots of $\ln(C_0/C)$ versus time in Fig. 6(i and ii), gave the rate constants for white light photolysis as listed in Table 1. The rate constants are larger for the white light since a larger range of wavelengths is employed. It is also possible with white light that heat is involved in the degradation process since near infrared light is involved. The Φ_P values are surprisingly larger for white light compared to Q band irradiation only for **1b**-AuNP and **1a**, Table 1.

In order to check if singlet oxygen is involved during photodegradation in white light, photobleaching experiments were performed in the presence of diazabicyclooctane (DABCO) a singlet oxygen scavenger. The photobleaching rate constant was calculated to be $8.71 \times 10^{-6} \text{ s}^{-1}$. This rate was slower than the rates listed in Table 1, confirming a significant singlet oxygen involvement in the mechanism. Thus, it is possible that both singlet oxygen and radicals are involved in the photobleaching mechanism.

3.4. Photocatalytic oxidation of cyclohexene

The possible oxidation products for cyclohexene have been reported before [3,9,10], they include cyclohexene oxide, cyclohexenol, cyclohexenone and cyclohexanediol. The products obtained in this work were confirmed by the spiking the photocatalysed samples with the respective standards. Control experiments were performed where cyclohexene was photo-oxidized in the absence of MPCs and MPC-AuNPs conjugates. The results for the control experiments showed negligible formation of the products. Similarly, in the absence of light but in the presence of TaPc derivatives (with or without AuNPs), no products were formed.

The main products obtained (and confirmed by spiking) are: cyclohexene oxide, 2-cyclohexen-1-ol, 2-cyclohexene-1-one and 1,2-cyclohexanediol. These are obtained as main products both by Q band and white light irradiations.

Table 1
Singlet oxygen and photobleaching quantum yields and rate constants for complexes **1a** and **1b** in the absence and presence of AuNPs in toluene.

Q band irradiation				White light		
MPc	Φ_Δ	Φ_P	$k \text{ (s}^{-1}\text{)}$	MPc	Φ_P	$k \text{ (s}^{-1}\text{)}$
1a	0.47	2.07×10^{-6}	7.16×10^{-5}	1a	2.27×10^{-6}	1.80×10^{-4}
1b	0.36	1.45×10^{-6}	7.35×10^{-5}	1b	1.17×10^{-6}	1.15×10^{-4}
1a -AuNP	0.75	2.45×10^{-6}	6.04×10^{-5}	1a -AuNP	2.36×10^{-6}	1.00×10^{-4}
1b -AuNP	0.88	1.02×10^{-6}	4.75×10^{-5}	1b -AuNP	1.59×10^{-6}	1.70×10^{-4}

Table 2
Percentage conversion of cyclohexene by complexes **1a**, **1b**, **1a**-AuNPs and **1b**-AuNPs in toluene. Photolysis time = 180 min.

MPc	Q band irradiation % Conversion ^a	White light % Conversion ^a
1a	24.2	48.1
1b	18.0	45.2
1a -AuNP	35.4	92.3
1b -AuNP	30.4	90.0

$$^a \text{ \%conversion} = \frac{(1 - \text{cyclohexene}_{\text{initial}}) - (1 - \text{cyclohexene}_{\text{remaining}})}{(1 - \text{cyclohexene}_{\text{initial}})} \times 100$$

Table 2 shows the percentage conversion of cyclohexene using complexes **1a**, **1b** and their conjugates with AuNPc as photocatalysts under Q band and white light irradiation. For experiments performed under Q band irradiation, the percentage conversion values were higher for **1a**-AuNPs and **1b**-AuNPs conjugates (35.4 and 30.4%, respectively), compared to **1a** and **1b** alone at 24.2 and 18.0%, respectively. This is associated with their increased singlet oxygen quantum yields compared to the TaPc complexes alone. Fig. 7 shows the variation of the percentage conversion over a period of 180 min. There is a fast increase in percentage conversion until ~50 min, after that there is slow or no increase. Complexes **1a**-AuNPs and **1b**-AuNPs gave the highest conversions at all times compared to complexes **1a** and **1b** in the absence of AuNPs. The reaction was also carried out in the presence of a singlet oxygen scavenger DABCO, Fig. 7(v). DABCO was added until there was no change in the GC trace of cyclohexene. The percentage conversion for complex **1a** after 180 min in the presence of DABCO was ~3.5% – this is small compared to complexes **1a** and **1b** and their conjugates in the absence of DABCO. The low percentage conversion in the presence of DABCO illustrates that singlet oxygen is the main agent involved in the photocatalytic oxidation of cyclohexene. However, the fact that there is a slight conversion of cyclohexene in the presence of DABCO suggests that it is not only singlet oxygen that is involved; there is a possibility of involvement of other reactive oxygen species. This was proved by doing photolysis in the presence of a free radical scavenger (benzoquinone) which showed a decrease of ~3.6% in percentage conversion, showing that free radicals are involved.

The percentage conversion values for catalytic reactions exposed to white light were high, Table 2. The values were 48.1%, 45.2%, 92.3% and 90.0% for **1a**, **1b**, **1a**-AuNPs and **1b**-AuNPs, respectively. The values were notably higher compared to Q band irradiation, however the complexes underwent considerable bleaching during catalysis (Fig. 8a) in the photocatalytic experiments involving white light. Less bleaching was observed on irradiation at the Q band, Fig. 8b. In the presence of AuNPs using white light (or Q band irradiation), the degradation of the TaPc derivatives was similar to that observed in Figs. 8a or b, respectively.

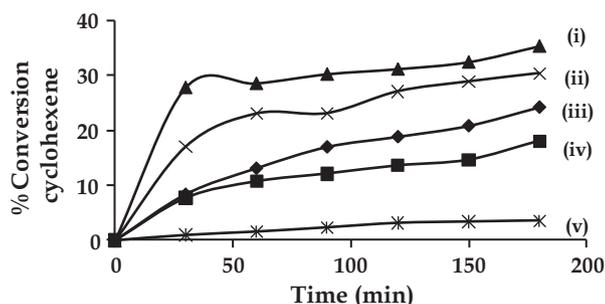


Fig. 7. Plots of percentage conversion plots of cyclohexene over a period of 180 min, where (i) is **1a**-AuNPs, (ii) **1b**-AuNPs, (iii) **1a**, (iv) **1b** and (v) **1a** in the presence of DABCO in toluene. Using Q band irradiation; [**1a**] = $2.80 \times 10^{-5} \text{ mol L}^{-1}$ or [**1b**] = $5.60 \times 10^{-5} \text{ mol L}^{-1}$, [cyclohexene] = 4.06×10^{-2} , DABCO = 0.0029 g/mL.

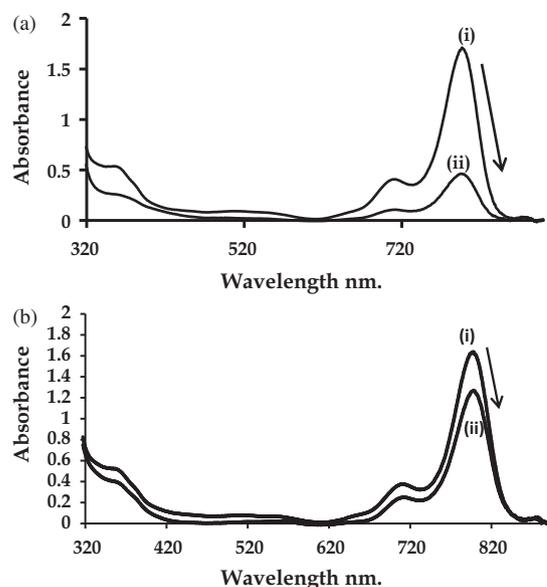


Fig. 8. Spectral changes observed for complex **1a** during the photocatalytic transformation of cyclohexene under (a) white light irradiation and (b) Q band irradiation. Irradiation over 180 min (i) before and (ii) after photolysis.

The alkyl substituents on the TaPc complexes are electron-donating and are prone to oxidative attack due to the increased electron density. Furthermore, the complexes conjugated with the AuNPs are prone to degradation as a result of SPR absorption and the increased singlet oxygen. However, in the presence of DABCO, Fig. 9(ii), photobleaching of the MPc complexes was minimal, compared to that without DABCO (Fig. 9(iii)) showing the involvement of singlet oxygen the photo-oxidation reactions).

Table 3 shows the product yields obtained for Q band irradiation in the presence of TaPc derivatives as photocatalysts and after 180 min of irradiation. The yields for the main products ranged from 6.3 to 21.2%, values which are higher than reported in literature [3], where the values of the same product ranged from 0.02% to 4.4% using ZnPc as a photocatalyst. Cyclohexene oxide has been reported as one of the minor products by Sehlotho et al. [3] using ZnPc as a photocatalyst. In this work cyclohexene oxide is a major product in the presence of **1a**-AuNPs.

Table 3 also shows percentage selectivity for the main products formed during the photocatalytic oxidation of cyclohexene under Q band and white light irradiations. Generally percentage selectivity values increased under white light experiments; however photobleaching of the MPc was a major drawback as discussed above. Alcohol is one of the desired products derived

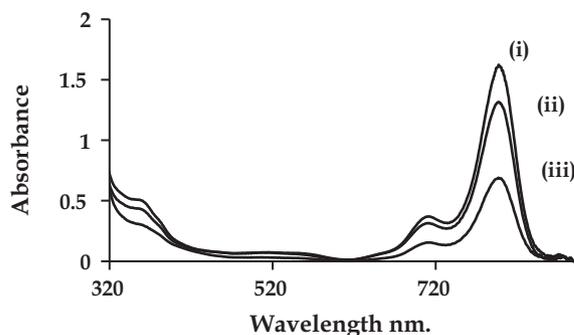


Fig. 9. Electronic absorption spectra for **1b** (i) before photoirradiation, (ii) after 180 min in the presence of DABCO and (iii) after 180 min in the absence of DABCO. [**1b**] = $5.6 \times 10^{-5} \text{ mol L}^{-1}$, [DABCO] = 0.0029 g/mL, Q band irradiation. Solvent = toluene.

Table 3

Percentage selectivity and product yield values for cyclohexene photocatalytic products. Photolysis time = 180 min.

MPC	Product	Q band irradiation % Selectivity ^a	White light % Selectivity ^a	Product yields under Q band irradiation (%) ^b
1a	Cyclohexene oxide	17.9	27.8	6.3
	2-Cyclohexen-1-ol	35.1	40.5	9.15
	2-Cyclohexene-1-one	26.2	38.0	8.6
	1,2-Cyclohexanediol	40.8	86.0	21.2
1b	Cyclohexene oxide	27.3	30.2	6.8
	2-Cyclohexen-1-ol	38.3	39.9	9.1
	2-Cyclohexene-1-one	35.1	52.2	11.8
	1,2-Cyclohexanediol	33.4	60.3	13.7
1a-AuNP	Cyclohexene oxide	46.0	50.8	11.5
	2-Cyclohexen-1-ol	20.4	29.8	6.7
	2-Cyclohexene-1-one	23.0	37.7	8.6
	1,2-Cyclohexanediol	30.1	34.0	7.7
1b-AuNP	Cyclohexene oxide	38.1	42.4	9.7
	2-Cyclohexen-1-ol	29.1	30.3	7.0
	2-Cyclohexene-1-one	27.3	77.3	17.5
	1,2-Cyclohexanediol	26.7	30.6	6.9

^a % selectivity = $\frac{\text{epoxide}_{\text{obtained}}}{[(1-\text{cyclohexene})_{\text{initial}} - (1-\text{cyclohexene})_{\text{final}}]}$

^b Based on the substrate cyclohexene.

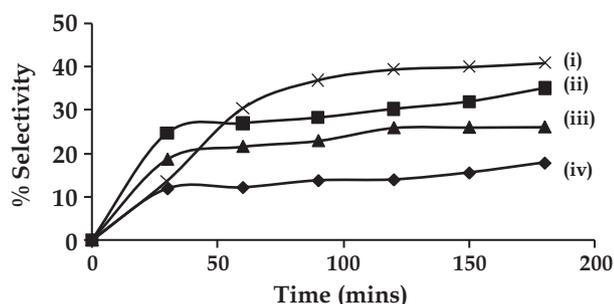


Fig. 10. Percentage selectivity plots of cyclohexene products in toluene using complex **1a**, where (i) is 1,2-cyclohexanediol, (ii) 2-cyclohexen-1-ol, (iii) 2-cyclohexene-1-one and (iv) cyclohexene oxide. $[\mathbf{1a}] = 2.80 \times 10^{-5} \text{ mol L}^{-1}$.

from oxidation of alkenes in the petrochemical industry. The percentage selectivity values for cyclohexenol (35.1% and 38.3%, for complexes **1a** and **1b**, respectively) under Q band irradiation, are higher than those reported for the photochemical oxidation of cyclohexene using sulfonated MPC (M = Pd, Al and Zn) [10], where percentage selectivity values ranged from 1.6 to 34.9% in the solvents: dimethylformamide:H₂O, dioxane:H₂O and acetonitrile. Figs. 10 and 11 show the percentage selectivity values over a period of 180 min for complexes **1a** and **1a**-AuNPs, respectively. The production of cyclohexene products, as shown in Figs. 10 and 11, was marked by a sweeping increase of products for the first 30 min,

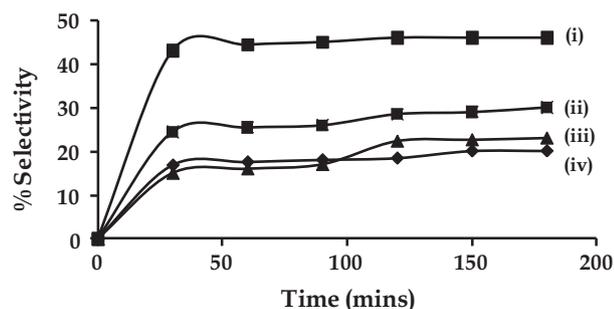
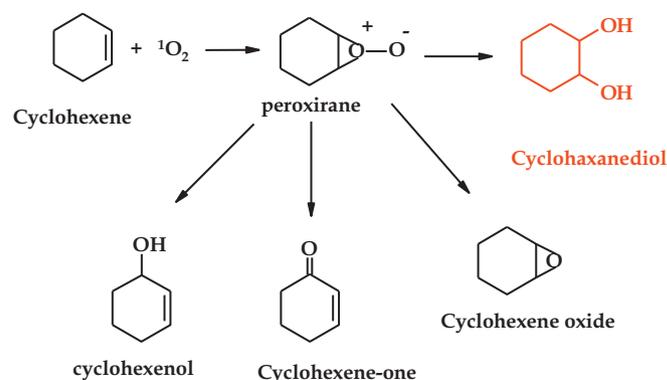


Fig. 11. Percentage selectivity plots of cyclohexene products in toluene using complex **1a**-AuNPs, where (i) is cyclohexene oxide, (ii) 2-cyclohexen-1-ol, (iii) 2-cyclohexene-1-one and (iv) 1,2-cyclohexanediol.



Scheme 2. Proposed mechanism for the formation of the photo-oxidation products.

followed by a slow production until photolysis was stopped at 180 min.

In literature, two major pathways are suggested for the sensitisation reactions by phthalocyanines. One is the energy transfer from an electronically excited complex to ground state molecular oxygen that subsequently yields singlet oxygen (Scheme 1). Another is the electron transfer from the excited complex to ground state molecular oxygen or reacting substrates thereby generating radicals such as superoxide radicals, Type I mechanism. As stated above, the % conversion of cyclohexene was slowed down in the presence of DABCO, Fig. 7, implying that singlet oxygen played a major role in photocatalytic oxidation. The mechanism proposed in this work is shown in Scheme 2 and is similar to that proposed by Sehlotho et al. [3]. Several reports [27–32] have shown that zwitterions, biradicals, endo-peroxides, peroxiranes are formed when ethylene interacts with singlet oxygen, hence the proposed mechanism in Scheme 2.

4. Conclusion

We have determined the stability of (OH)₃TaPc complexes and (OH)₃TaPc in the presence of AuNPs under different conditions (white and Q band irradiation). The complexes were more stable under Q band irradiation. The singlet oxygen production was improved significantly by the presence of AuNPs. Photocatalytic oxidation of cyclohexene was carried out successfully. The percentage conversion of cyclohexene was improved by the presence

of gold nanoparticles. Percentage selectivity values were generally improved when compared to literature values. Similarly, the percentage yields were improved significantly.

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