



# Photooxidation of 4-chlorophenol sensitized by lutetium tetraphenoxy phthalocyanine anchored on electrospun polystyrene polymer fiber

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## ARTICLE INFO

### Article history:

Received 27 July 2011

Accepted 7 November 2011

Available online 15 November 2011

### Keywords:

Lutetium phthalocyanine

Electrospinning

Chlorophenol

Photocatalysis

## ABSTRACT

An electrospun polystyrene (PS) fiber incorporating tetraphenoxy phthalocyanine complex of lutetium (LuTPPc/PS) as a photosensitizer was applied for the degradation of 4-chlorophenol in aqueous solution in the presence of visible light. The photocatalytic activity of the LuTPPc in the fiber was compared to that of zinc phthalocyanine (ZnPc) incorporated into the PS fiber, and the former showed higher activity. UV–Vis spectral changes of sample solutions indicated transformation of the analyte with first order kinetics and half-lives that are within one and half hours for LuTPPc/PS. Products identified from the spectral changes and gas chromatography were benzoquinone, hydroquinone and 4,4'-dihydroxydiphenol suggesting that the photodegradation of 4-chlorophenol was through both Types I and II mechanisms.

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## 1. Introduction

Photocatalysis has been recognized as a promising technique for water and air purification and has since been studied extensively as an alternative to currently used technologies, such as chlorination, ozonation and adsorption on active carbon [1,2]. There have been reports of photocatalysis involving inorganic compounds that use the ultra violet (UV) part of the solar spectrum [3,4].

There has been a growing interest in the use of dyes such as phthalocyanines (Pcs) in photosensitized catalytic applications [5,6]. This is due to their excellent absorption of visible light [7], high stability and remarkable photoactivity [8]. Most importantly, the ability of some of these phthalocyanines to efficiently produce reactive singlet oxygen from ground state molecular oxygen in the presence of light is of much interest since singlet oxygen is a good candidate for oxidative processes [9]. However, most of the reported photosensitized reactions involving phthalocyanines usually occur in homogeneous media, thus rendering recycling of the phthalocyanine very difficult. There have been attempts to anchor these phthalocyanines onto insoluble support systems such as amberlite [10,11], silica and zeolite [6] as well as polycrystalline titanium oxide [12] for heterogeneous catalysis. Anchoring of phthalocyanines onto electro-spun nanofibers for use in photocatalysis has not been explored. These nanofabric materials have the advantage of large surface area that would enhance the catalytic activity of the phthalocyanine immobilized on them.

Functionalisation of nanofibers through the integration of functional molecules into solid polymer fiber core has been found to be desirable in many fields such as biosensor technology [13], tissue engineering [14], drug delivery [15] and nanoelectronics [16] due to the large surface area of these nanofibers. Incorporation of phthalocyanines into electro-spun polymer fibers has been reported with the functionality of the phthalocyanine maintained in the solid fiber core [17,18]. Mosinger et al., reported that a ZnPc anchored on polyurethane polymer fiber led to a red shifted Q-band compared to those recorded in some solvents [19]. Such a red shift is desirable and very promising in harvesting visible light for applications in photosensitized catalysis.

Chlorophenols are very common aqueous organic pollutants, partly because of their importance in the production of fungicides and herbicides. They are also present in effluents of pulp mills. As a result of the immense economic importance associated with the removal of chlorophenols during water purification, various attempts to oxidize these pollutants have been described [20,21].

There has been considerable investigation into the degradation of phenols using oxidants in the presence of catalysts such as metallophthalocyanines (MPcs). The use of oxidants in the degradation of chlorophenols (and related molecules) to less harmful products has proven to be successful [22–26]. However, processes involving no oxidants are still preferred to avoid the harmful effects of the toxic oxidants.

In this paper we demonstrate the photosensitized oxidation ability of a phthalocyanine anchored onto a polystyrene polymer fiber in the degradation of 4-chlorophenol as model organo-chlorinated pollutant. Tetraphenoxy-phthalocyanine complex of lutetium(III) (LuTPPc, Fig. 1) was anchored onto a polystyrene (PS) polymer fiber by electrospinning. The choice of lutetium was

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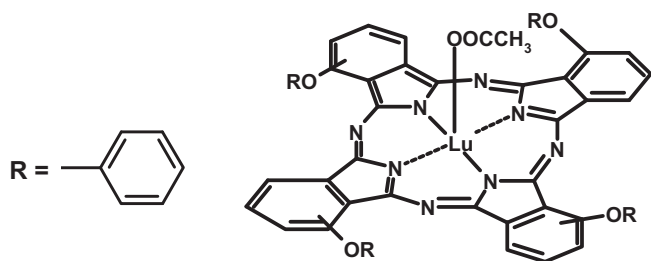


Fig. 1. Molecular structure of LuTPPc.

influenced by its larger size which will encourage intersystem crossing to the triplet state, hence generating singlet oxygen which is required for photocatalysis. Also the applications of the lanthanide phthalocyanines in photocatalysis are still rare in the literature. The bulky substituent was chosen to minimize aggregation which is a major problem with phthalocyanines. The photocatalytic activity of the LuTPPc/PS is compared with that of a simple MPc using zinc phthalocyanine (ZnPc/PS) as an example.

## 2. Experimental

### 2.1. Materials

Polystyrene (PS, Mw = 192,000 g/mol), *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were from MERCK Chemical Ltd, anthracene-9,10-bis-methylmalonate (ADMA), 1,4-benzoquinone 98%, zinc phthalocyanine (ZnPc) and sodium azide 99%, sodium hydroxide/di-sodium hydrogen phosphate were from Aldrich. 1-Pentanol was from SAARCHEM. 4-Chlorophenol 99% was from Fluka while hydroquinone was obtained from May and Baker LTD.

### 2.2. Synthesis

The synthesis of LuTPPc has been reported [27] and its molecular structure is shown in Fig. 1. The electrospinning technique with or without Pc complexes has been described [17,18,28]. For the current work, the LuTPPc/PS or ZnPc/PS electrospun fiber was formed as follows: a solution containing 2.5 g ( $1.3 \times 10^{-5}$  moles of polystyrene and 1.35 mg ( $1.2 \times 10^{-6}$  moles) of LuTPPc (or ZnPc) in 10 ml DMF/THF(4:1) was stirred for 24 h to produce a homogeneous solution. The solvent mixture was employed to allow both PS and LuTPPc (ZnPc) to dissolve. The solution was then placed in a cylindrical glass tube fitted with a capillary needle. A potential difference of 20 kV (–5 to 15 kV) was applied to provide the charge for the spinning process. The distance between the cathode (static fiber collection point) and anode (tip of capillary needle) was 15 cm with pump rate maintained at 1 mL/h. The flow rate was, however, increased to 2 mL/h in the case of the polystyrene/phthalocyanine composite to avoid clogging of the needle.

### 2.3. Equipment

Scanning electron microscope (SEM) images of the fiber alone or in the presence of LuTPPc were obtained using a JOEL JSM 840 scanning electron microscope. The fiber diameters were measured using Cell<sup>^</sup>D software from Olympus. The average diameter of seventy different fibers was taken.

Raman data was obtained using a Bruker Vertex 70-Ram II spectrometer equipped with a Nd:YAG laser that emit at 1064 nm and liquid nitrogen cooled germanium detector.

The GAUSSIAN 03 programme [29] running on an Intel/Linux cluster was used to perform DFT calculations. The calculations were

done at the B3LYP/6-31G(d) level for geometry optimization and excited energy calculations (TDDFT). All visualization used the GAUSSVIEW 4.1 program.

### 2.4. Singlet oxygen quantum yield determination of LuTPPc in the fiber mat

A chemical method was employed for the determination of the singlet oxygen quantum yield of the LuTPPc or ZnPc modified fibers in water. The singlet oxygen quantum yield ( $\Phi_{\Delta}$ ) determinations were carried out in aqueous solutions using ADMA as the quencher (absorbance  $\sim 0.542$  at 380 nm). The modified fiber, LuTPPc (or ZnPc)/polystyrene (10 mg) was suspended (as small pieces) in this solution and irradiated using a set-up consisting of a General Electric Quartz lamp (300 W), 600 nm glass (Schott) and water filters, to filter off ultra-violet and far infrared radiations respectively. An interference filter at 670 nm with bandwidth of 40 nm was placed in the light path just before the cell containing the sample. The ADMA quantum yield  $\Phi_{ADMA}$  was calculated using Eq. (1), while the extinction coefficient of ADMA in water has been reported as  $\log(\epsilon) = 4.1$  [30].

$$\Phi_{ADMA} = \frac{(C_0 - C_t)V_R}{I_{abs}t} \quad (1)$$

where  $C_0$  and  $C_t$  are the ADMA concentrations prior to and after irradiation, respectively;  $V_R$  is the solution volume;  $t$  is the irradiation time per cycle and  $I_{abs}$  is defined by Eq. (2).

$$I_{abs} = \frac{\alpha I}{N_A} \quad (2)$$

where  $\alpha = 1 - 10^{-A(\lambda)}$ ,  $A(\lambda)$  is the absorbance of the sensitizer at the irradiation wavelength,  $A$  is the irradiated area ( $2.5 \text{ cm}^2$ ),  $I$  is the intensity of light ( $4.52 \times 10^{16} \text{ photons cm}^{-2} \text{ s}^{-1}$ ) and  $N_A$  is Avogadro's constant.

The absorbance used for Eq. (2) is that of the LuTPPc (or ZnPc) on the fiber (not in solution) measured by placing the fiber on a glass plate. The light intensity measured refers to the light reaching the spectrophotometer cell, and it is expected that some of the light may be scattered, hence the  $\Phi_{\Delta}$  value of the LuTPPc (or ZnPc) on the fiber is an estimate. The UV–Vis spectrum of the modified fiber was obtained by placing it directly on the glass plate using a Shimadzu UV-2550 spectrophotometer.

The singlet oxygen quantum yields  $\Phi_{\Delta}$  were calculated using Eq. (3) [31]

$$\frac{1}{\Phi_{ADMA}} = \frac{1}{\Phi_{\Delta}} + \frac{1}{\Phi_{\Delta}} \cdot \frac{k_d}{k_a} \cdot \frac{1}{[ADMA]} \quad (3)$$

where  $k_d$  is the decay constant of singlet oxygen and  $k_a$  is the rate constant of the reaction of ADMA with  $O_2(^1\Delta_g)$ . The intercept obtained from the plot of  $1/\Phi_{ADMA}$  versus  $1/[ADMA]$  gives  $1/\Phi_{\Delta}$ .

### 2.5. Photocatalytic reactions

Photocatalytic reactions were carried out in a magnetically stirred batch reactor (glass vial). The irradiation experiments were carried out using the photolysis set-up described above for singlet oxygen detection. The intensity of the light reaching the reaction vessel was measured with a power meter (POWER MAX 5100, Molelectron Detector Inc) and found to be  $3.5 \times 10^{20} \text{ photons cm}^{-2} \text{ s}^{-1}$ . The transformation was monitored by observing the absorption bands of 4-chlorophenol after each photolysis cycle of 15 min using a Shimadzu UV-2550 spectrophotometer. The experiments were carried out using a variety of concentrations of 4-chlorophenol in pH 11 phosphate buffer. Each sample solution contained 10 mg of functionalized fiber.

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