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Photocatalytic behavior of phthalocyanine-silver nanoparticle conjugates supported on polystyrene fibers

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ABSTRACT

Herein, carbazole derivatized non-peripheral (1,(4)-tetra(carbazol-2-yloxy)phthalocyaninatozinc(II), 3-TCbZnPc) and peripheral (2,(3)-tetra(carbazol-2-yloxy)phthalocyaninato zinc(II), 4-TCbZnPc) are conjugated to silver nanoparticles and their photochemical and photophysical behavior are reported. The presence of silver nanoparticles resulted in reduced fluorescence, and increased triplet and singlet oxygen quantum yields. The conjugates were further electrospun into polystyrene fibers, and employed for the photodegradation of methyl orange. The photodegradation of methyl orange using all functionalized fibers followed first order kinetics, and was faster when the conjugates with silver nanoparticles were used. The non-peripherally substituted 3-TCbZnPc gave better photocatalytic activity compared to its peripherally substituted counterpart (4-TCbZnPc). The hybrid electrospun fibers provide great potential as active photocatalysts for degrading organic pollutants.

1. Introduction

Phthalocyanines (Pcs) have found applications in different fields as dyes and pigments [1], in nonlinear optics [2], as electrocatalysts [3], and in photodynamic therapy of cancer [4,5]. One of the interesting features of phthalocyanine is their ability to generate cytotoxic singlet oxygen responsible for the destruction of many recalcitrant pollutants in waste water, and in the destruction of cancer cells [6–8].

On the other hand, nanoparticles have been reported to enhance the photocatalytic activity and singlet oxygen quantum yields of the phthalocyanines [9,10]. This is due to the heavy atom effect which encourages intersystem crossing to the triplet state. It is from this triplet state that there is energy transfer to molecular oxygen forming the cytotoxic singlet oxygen. We have recently reported on improved photodegradation of pollutants by phthalocyanines in the presence of magnetic or gold nanoparticles [11,12]. In this work, phthalocyanines are employed in the presence of silver nanoparticles (which have antimicrobial properties), as photocatalysts for the photodegradation of methyl orange (an azo dye). Azo dyes are of great environmental concern since large amounts of dyes may enter the wastewater streams during industrial operation [13]. They are easily converted into the corresponding aromatic amines, which can cause cancer [13,14]. TiO_2 doped with phthalocyanine has been employed for the degradation of methyl orange using visible light [15]. However, TiO_2 absorbs weakly in the visible region. We have recently reported on the photocatalytic degradation of methyl orange using phthalocyanines in the absence of nanoparticles [16]. This work reports on the photocatalytic behavior of previously synthesized zinc phthalocyanine complexes, tetrasubstituted with carbazole functionality (Fig. 1A [17,18]), in the presence of silver nanoparticles (AgNPs). AgNPs have been found to improve the photophysicochemical behavior of phthalocyanines [19,20]. This is the first time that silver nanoparticles are employed together with MPcs for improved photocatalysis. The presence of silver nanoparticles results in both increased triplet quantum yields and lifetimes, which is an advantage in efficiently generating singlet oxygen quantum yields, which is involved in the photodegradation of methyl orange.

Ease of recovery and recyclability of a photocatalyst following use in photodegradation is an important aspect in catalysis [21]. Phthalocyanines have been embedded in various supports such as zeolites and single walled carbon nanotubes for heterogeneous catalysis purposes [22–24]. Another method of supporting phthalocyanines for heterogeneous catalysis is immobilizing them onto electrospun fibers. The method offers a number of advantages such as the large surface area for

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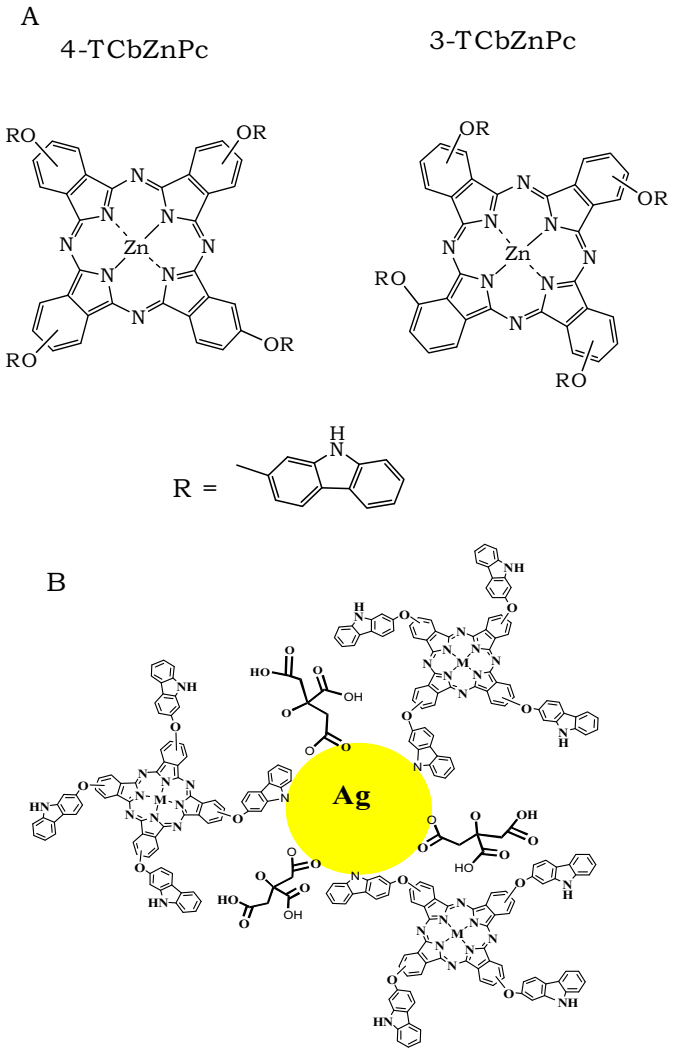

Fig. 1. Molecular structures of 3-TCbZnPc and 4-TCbZnPc (A), and the schematic representation of the interaction between silver nanoparticles and the phthalocyanine (B).

the adsorption of the dye, which implies greater availability of the dye for degradation. Hence, eletrospun fibers are employed in this work. Phthalocyanines have been supported onto electrospun fibers for the photodegradation of pollutants with the functionality of the phthalocyanine maintained [25]. We compare the effects of peripheral (2,(3)-tetra(carbazol-2-yloxy)phthalocyaninatozinc(II), 4-TCbZnPc) and non-peripheral (1,(4)-tetra(carbazol-2-yloxy)phthalocyaninatozinc(II), 3-TCbZnPc) substitution on the photodegradation of methyl orange when in electrospun fibers (using polystyrene, PS) or in solution. The photocatalyst combinations used in this work when electrospun into PS are: 4-TCbZnPc/PS, 4-TCbZnPc-AgNPs/PS, 3-TCbZnPc/PS and 3-TCbZnPc-AgNPs/PS.

2. Experimental

2.1. Materials

Polystyrene (PS, Mw = 192,000 g/mol), anthracene-9,10-bis-methylmalonate (ADMA), dimethylsulfonoxide (DMSO), pH 9.2 buffer tablets, Zn phthalocyanine, 1,3-diphenylisobezofuran (DPBF) and Sephadex® G-25 were from Sigma–Aldrich. The syntheses of 2,(3)-tetra(carbazol-2-yloxy)phthalocyaninatozinc(II) (4-TCbZnPc) and 1,(4)-tetra(carbazol-2-yloxy)phthalocyaninatozinc(II) (3-TCbZnPc) have been reported before [17,18]. AgNPs were also synthesized as reported in the literature [26].

2.2. Equipment

Ground state absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorimeter. The absorbance for fluorescence studies (at the excitation wavelength 612 and 625 nm for 4-TCbZnPc-AgNPs and 3-TCbZnPc-AgNPs, respectively) ranged between 0.05 and 0.1.

Fluorescence lifetimes were measured using a time correlated single photon counting (TCSPC) setup (FluoTime 200, Picoquant GmbH). The excitation source was a diode laser (LDH-P-670 driven by PDL 800-B, 670 nm, 20 MHz repetition rate, 44 ps pulse width, Picoquant GmbH). Details have been provided before [27].

Scanning electron microscope (SEM) images of AgNPs/PS, 4-TCbZnPc/PS, 4-TCbZnPc-AgNPs/PS, 3-TCbZnPc/PS and 3-TCbZnPc-AgNPs/PS were obtained using a JOEL JSM 840 scanning electron microscope. Transmission electron microscope (TEM) images for AgNPs or AgNPs/Pc conjugates were obtained using a Carl Zeiss Libra transmission electron microscope, at 100 kV accelerating voltage.

A laser flash photolysis system was used for the determination of triplet decay kinetics. The excitation pulses were produced by a Quanta-Ray Nd:YAG laser (1.5 J/9 ns), pumping a Lambda Physik FL 3002 dye laser (Pyridin 1 in methanol), as described before [17]. Triplet lifetimes were determined by exponential fitting of the kinetic curves using OriginPro 8 software. For triplet state studies, argon was bubbled through the solution to remove oxygen. The absorbance for triplet state studies was 1.5.

Photo-irradiation for singlet oxygen quantum yield determinations for 4-TCbZnPc/PS, 4-TCbZnPc-AgNPs/PS, 3-TCbZnPc/PS and 3-TCbZnPc-AgNPs/PS in water were carried out using a General Electric Quartz line lamp (300 W). 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, 670 nm with a band width of 40 nm) was additionally placed in the light path before the sample. Light intensity was measured with a POWER MAX 5100 (Molelectron detector incorporated) power meter, and was found to be 9.53×10^{18} photons s^1 cm^{-2}. This set-up was also used for the photodegradation of methyl orange.

The phosphorescence of singlet oxygen at 1270 nm was used to determine the singlet oxygen quantum yield of 4-TCbZnPc, 4-TCbZnPc-AgNPs, 3-TCbZnPc and 3-TCbZnPc-AgNPs in DMSO. For these studies, an ultra-sensitive germanium detector (Edinburgh Instruments, EI-P) combined with a 1000 nm long pass filter (Omega, RD 1000 CP) and a 1270 nm band-pass filter (Omega, C1275, BP50) were used. The singlet oxygen phosphorescence signal was compared with that of the ZnPc standard. The absorbance of the Pc and its conjugate for these studies was 1.5.

2.3. Photophysical and photochemical parameters

Fluorescence (Φ_f) and triplet (Φ_T) quantum yields were determined in DMSO using methods described before [28,29] using ZnPc as a standard ($\Phi_f = 0.20$ [28] and $\Phi_T = 0.65$ [29]). Singlet oxygen quantum yields (Φ_Δ) for 4-TCbZnPc, 4-TCbZnPc-AgNPs, 3-TCbZnPc and 3-TCbZnPc-AgNPs were determined using the phosphorescence of singlet oxygen at 1270 nm [30], Eq. (1):

$$I(t) = B\frac{\tau_D}{\tau_T - \tau_D}[e^{-t/\tau_T} - e^{-t/\tau_D}] \quad (1)$$