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Photophysicochemical behavior and antimicrobial activity of dihydroxosilicon tris(diaquaplatinum)octacarboxyphthalocyanine

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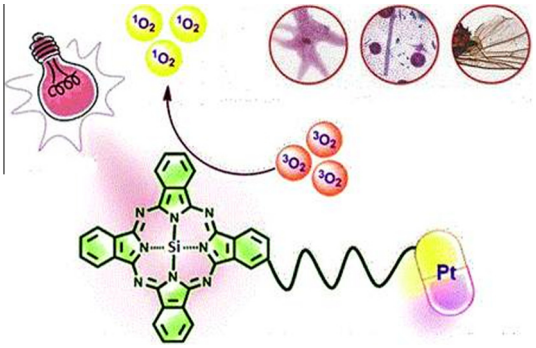
HIGHLIGHTS

- Platination of dihydroxosilicon octacarboxy phthalocyanine have been established.
- Improved photophysical activity due to presence of platinum was demonstrated.
- Additive effect of photodynamic activity of silicon phthalocyanine and cytotoxicity of platinum was discussed.
- High antimicrobial activity under illumination towards *Candida albicans* and *Escherichia coli* by the conjugate was established.

GRAPHICAL ABSTRACT



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ABSTRACT

Platination of dihydroxosilicon octacarboxyphthalocyanine $(OH)_2SiOCPc$ was successfully carried out to give dihydroxosilicon tris(diaquaplatinum)octacarboxyphthalocyanine $(OH)_2SiOCPc(Pt)_3$ conjugate. Slight blue shifting of the absorption spectrum of $(OH)_2SiOCPc(Pt)_3$ was observed on conjugation with platinum. Comparative photophysicochemical behavior and antimicrobial photo-activities of $(OH)_2SiOCPc(Pt)_3$ conjugate with $(OH)_2SiOCPc$ or Pt nanoparticles revealed that the heavy atom, Pt on the periphery of the phthalocyanine significantly enhanced its singlet oxygen generation with a quantum yield of 0.56 obtained for the $(OH)_2SiOCPc(Pt)_3$ conjugate. The $(OH)_2SiOCPc(Pt)_3$ conjugate showed highest antimicrobial activity towards *Candida albicans* and *Escherichia coli* compared to $(OH)_2SiOCPc$ and Pt nanoparticles alone under illumination.

Introduction

Cis-diamine derivatives of platinum complexes have been reported as cytotoxic agents in chemotherapy of cancer though there are still few challenges due to poor selectivity in tumors [1]. There have been great prospects shown in light sensitized activity of metallophthalocyanines (MPcs) in non-invasive treatment of superficial tumors through photodynamic therapy (PDT) of cancer [2] and in the photoinactivation of bacteria or viruses [3,4] through photodynamic antimicrobial chemotherapy (PACT). This is due to the MPcs intense absorption in the red region of visible light, selective localization in cells and efficient generation of singlet oxygen ($^1O_2$) [5]. Recently, selective accumulation in tumor cells of Pt(II) complexes was shown to improve when they were covalently conjugated with porphyrin analogs [6–8]. The conjugates showed a synergistic effect of photodynamic activity of the porphyrins and

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cytotoxicity of platinum. Consequently, some covalent conjugates of Pt complexes with porphyrin-like tetraazamacrocycles, MPcs have been reported [9–11]. Recently, we reported on the aluminum carboxy metallophthalocyanine-Pt conjugate being the first report on conjugates of Pt and MPcs with a diamagnetic central metal [12]. MPc derivatives in which the central metal is diamagnetic and non-transitional are photoactive, and are often employed in photosensitization [13]. Silicon phthalocyanines (SiPcs) are known photosensitizers for PDT and are in clinical trials [14,15]. For photodynamic applications, water solubility plays a very important role for potential photosensitizers [16] and as said above, photodynamic applications can occur through PACT. PACT is a process that utilizes a similar concept as PDT [17] in that a combination of light and a photosensitizer produces cytotoxic oxygen species that kills bacterial cells. PACT can be applied with high efficiency for inactivation of pathogenic microorganisms which are resistant to antibiotics [17] hence, we report herein on the photophysicochemical properties of water soluble conjugate of silicon phthalocyanine with diaquaplatinum; dihydroxosilicon tris(diaquaplatinum)octacarboxyphthalocyanine, $(OH)_2SiOCPc(Pt)_3$ (**2**) (Scheme 1) and its photoinactivation of *Escherichia coli* (E.C.), a bacterium and *Candida albicans* (C.A.), a fungus; relative to silicon octacarboxyphthalocyanine $(OH)_2SiOCPc$ (**1**) (Scheme 1) or Pt nanoparticles. We have recently reported on the inactivation of *Staphylococcus aureus* using zinc phthalocyanines in solution and in the presence of Ag or Au nanoparticles [18,19]. Unsymmetrical zinc phthalocyanine in solution has also been reported to show photo-inhibition of *C. albicans* [20] while unsubstituted phthalocyanine has shown inactivation of *E. coli* [21]. This work therefore explores the additive effect of photodynamic activity of $(OH)_2SiOCPc$ and cytotoxicity of Pt in $(OH)_2SiOCPc(Pt)_3$ conjugate.

Experimental

Materials

Potassium hexachloroplatinate(IV) and zinc phthalocyanine (ZnPc) were purchased from Aldrich. Sodium hydroxide was purchased from Saarchem. Dihydroxosilicon octacarboxyphthalocyanine $(OH)_2SiOCPc$ was synthesized according to modified literature methods [22] and its sodium salt was synthesized according to methods employed for other metal octacarboxy phthalocyanines [23]. Potassium tetrachloroplatinate(II) was synthesized from potassium hexachloroplatinate according to modified literature methods [10]. Platinum nanoparticles used in this work for comparative/control study were also synthesized, purified and characterized according to literature method [12]. Agar bacteriological BBL Mueller Hinton broth and nutrient agar were purchased from Merck. *E. coli* (E.C.) and *C. albicans* (C.A.) were purchased from Microbiologics. AlPcSMix (a mixture of aluminum phthalocyanine sulfonates), used as a standard for the determination of singlet oxygen quantum yields in water, was synthesized according to literature methods [24].

Equipment

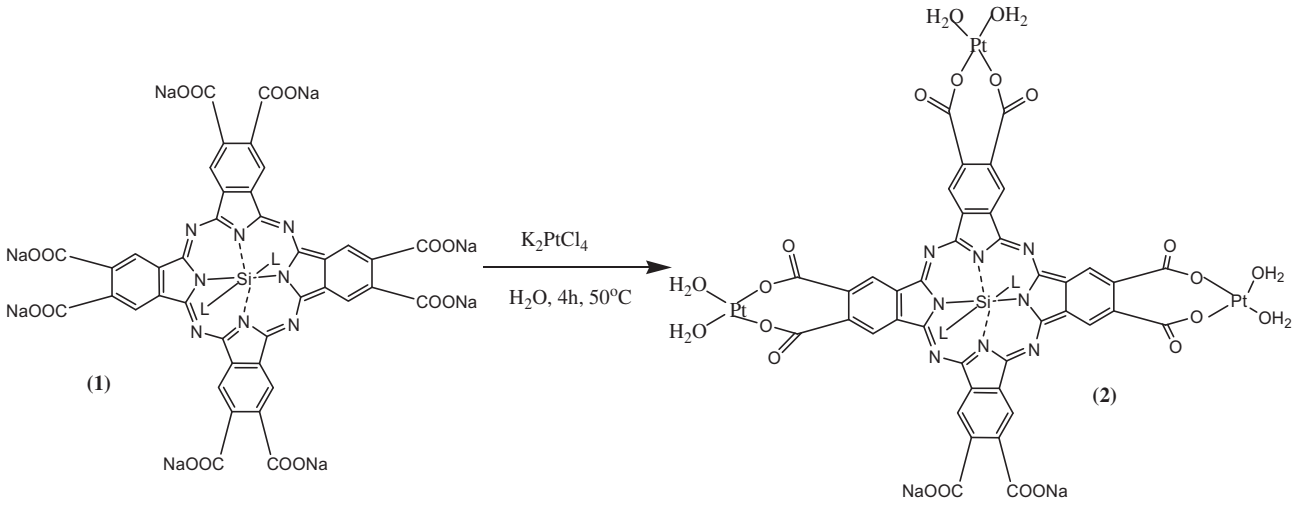
Ground state electronic absorption spectra were recorded on Shimadzu UV-2550 spectrophotometer and infrared spectra on Perkin Elmer Spectrum 100 FT-IR spectrometer. Transmission electron microscopy (TEM) images were obtained using a ZEISS LIBRA® JEOL JEM 1210 transmission electron microscope at 100 kV acceleration voltage and Energy dispersive spectroscopy (EDS) was done on an INCA PENTA FET couple to the VAGA TESCAM using 20 kV acceleration voltage.

Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorimeter. Fluorescence lifetimes were measured using a time correlated single photon counting (TCSPC) setup (FluoTime 200, Picoquant GmbH). Details have been provided before [25].

X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 Discover equipped with a Lynx eye detector, using Cu-Kα radiation (1.5405 Å, nickel filter), as described before [25].

Time resolved phosphorescence of singlet oxygen at 1270 nm was used to determine the singlet oxygen quantum yield. The dynamic phosphorescence decay of singlet oxygen ($^1O_2$) was demonstrated using its phosphorescence at 1270 nm. Details have been provided before [26]. The data obtained was analyzed using ORIGIN PRO 8 software. The $^1O_2$ phosphorescence signal was compared with an AlPcSMix standard.

Mass spectral data were collected with a Bruker AutoFLEX III Smartbeam TOF/TOF Mass spectrometer. The instrument was operated in positive ion mode using a *m*/*z* range of 500–3000 amu. The voltage of the ion sources were set at 19 and 16.7 kV for ion sources 1 and 2 respectively, while the lens was set at 8.50 kV. The reflector 1 and 2 voltages were set at 21 and 9.7 kV respectively. The spectra were acquired using alpha-cyano-4-hydroxycinnamic acid as the MALDI matrix, and a 355-nm Nd-YAG laser as the ionizing source.



Scheme 1. Synthesis of dihydroxosilicon tris(diaquaplatinum)octacarboxyphthalocyanine ($(OH)_2SiOCPc(Pt)_3$).