



# Enhanced Light-Driven Antimicrobial Activity of Cationic Poly(oxanorbornene)s by Phthalocyanine Incorporation into Polymer as Pendants

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Amphiphilic poly(oxanorbornene)s are promising synthetic polymers that mimic the structural properties and antimicrobial functions of naturally occurring antimicrobial peptides. Here, poly(oxanorbornene)s bearing pendant zinc(II) phthalocyanine and triphenyl(ethyl) phosphonium functionalities are synthesized by ring-opening metathesis polymerization (ROMP). Fluorescence, singlet oxygen and triplet quantum yields of polymers are measured in dimethyl sulfoxide and aqueous medium. The singlet oxygen quantum yields of copolymers with the highest triphenyl and triethyl phosphonium content are found to be 0.29 and 0.41, respectively. Then, antimicrobial activities of polymers against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) are investigated under both dark and light conditions. Synergistic effect of zinc(II) phthalocyanine and phosphonium-containing poly(oxanorbornene) is observed that the conjugate possessing the most triphenyl phosphonium side chains has the highest activity under light against both gram-positive and gram-negative bacterial strains after 80 min irradiation, reducing the survival of *E. coli* or *S. aureus* by 99.9999%. Hemolytic concentrations of the copolymers are found between 8 and 512  $\mu\text{g mL}^{-1}$ . Scanning electron microscopy (SEM) proves that the bacteria membrane deforms after contacting with the biocidal polymer.

## 1. Introduction

Both cancer and infections caused by antibiotic resistant microorganisms are serious problems for public health in today's world. Therefore, the scientific community has been studying how to overcome the problem of cancer and microbial drug resistance in recent years.<sup>[1]</sup> Photodynamic therapy (PDT) and photodynamic antimicrobial chemotherapy (PACT) are alternative methods for the treatment of these diseases. These methods involve the use of photosensitizers to generate reactive oxygen species (ROS) upon light exposure at an appropriate wavelength and, in this sense, phthalocyanine (Pc) has properties such as relatively high extinction coefficient, excellent visible/near-infrared absorption to act as phototherapeutic agent. The attachment of various substituents to the peripheral or/and non-peripheral positions of phthalocyanine and also metallation yield new materials with the necessary functions for specific application areas.<sup>[2]</sup> For instance, peripherally or

non-peripherally substituted zinc phthalocyanines (ZnPcs) have the ability to generate ROS and have been used or tested as photosensitizers in various medical applications for the treatment of cancer by photodynamic therapy, photodynamic inactivation of microorganisms, and theranostic purposes.<sup>[3]</sup> Similarly, functionalization of polymeric materials with phthalocyanine allows the electronic, optical, and catalytic properties of phthalocyanine to be incorporated within a polymer and these materials can be used different purposes, e.g., electrocatalysis,<sup>[4]</sup> electrochromism,<sup>[5]</sup> antitumoral and antimicrobial photodynamic therapy,<sup>[6]</sup> bulk heterojunction organic solar cells.<sup>[7]</sup>

Phthalocyanine-containing polymers are generally defined by the way in which the macrocycle is incorporated within the macromolecular structure as either network, main-chain or side-chain polymers.<sup>[8]</sup> There are three general methods for the incorporation of phthalocyanines as pendant groups into polymers. These are (i) the grafting of a preformed phthalocyanine derivative to a preformed polymer, (ii) a statistical condensation involving a polymer bound precursor and (iii) the

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