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# Photophysicochemical behaviour and antimicrobial properties of monocarboxy Mg (II) and Al (III) phthalocyanine-magnetite conjugates

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ABSTRACT

Asymmetric Mg (II) or Al (III) phthalocyanine (containing a COOH group and 3-pyridylsulfanyl units) was conjugated via an amide bond to amino functionalized magnetic nanoparticle (AIMN) to form MgPc-AIMN or AlPc-AIMN conjugate, and characterized. The photophysicochemical behaviour of the phthalocyanine–AIMN conjugates was investigated and compared to the asymmetric Pcs and to the simple mixture of Pc with AIMNs without a chemical bond, (MPc-AIMN (mixed)). The directed covalent linkage of AIMNs to the asymmetrical metallopthalocyanines afforded improvements in the singlet oxygen ($\Phi_\Delta$) and triplet state quantum yield ($\Phi_T$) as well as singlet oxygen lifetimes for the MPcs–AIMN-linked conjugates compared to MPc-AIMN (mixed) and MPcs alone. The asymmetric phthalocyanines and their conjugates showed effective antimicrobial activity against *Escherichia coli* bacteria under illumination.





## 1. Introduction

Iron oxide magnetic nanoparticles particularly magnetite ($Fe_3O_4$) are the most prominent class of magnetic nanoparticles with potential application in hyperthermia, drug delivery, bio sensing, cell separation and magnetic resonance imaging [1–3] due to their biocompatibility, ease of injection into targets and high level accumulation in target tissues [4–7]. Surface functionalized magnetic nanoparticles can attach to other compounds via conjugation to produce bifunctional nanocomposites [8] which can be directed to specific tissues or organs using an external magnetic field [9,10].

Metallophthalocyanines (MPcs) have shown great prospects in their light sensitized activity through photodynamic therapy (PDT) of cancer [11] owing to their intense absorption in the red region of visible light, selective localization in cells and efficient generation of singlet oxygen ($^1O_2$) [12]. Studies have revealed that they can also be effective in the photoinactivation of microorganisms [13,14] through photodynamic antimicrobial chemotherapy (PACT) and can become an alternative for the obliteration of emerging microorganisms' strains in both clinical and environmental applications [15–17].

There have been some studies on the improved photophysical abilities of MPcs when mixed or linked with iron oxide magnetic nanoparticles [18–21]. Most of these literature reports were obtained with tetrasubstituted symmetrical MPcs that allowed all four peripheral substituents for linkage with the nanoparticles, which can be non-directional. Recently, effective PDT capabilities of asymmetrical porphyrin analogs were shown to improve when they formed nanomagnet hybrids with iron oxide nanoparticles [22]. The nanomagnets showed a synergistic effect of photodynamic activity of the porphyrins and ease of recovery after use owing to the magnetic nanoparticles. Subsequently, we reported a covalent conjugate of iron oxide nanoparticles with asymmetric indium phthalocyanine carrying monoamino group, which exhibited high efficiency for PACT [23]. These studies imply that directional covalent linking of iron oxide magnetic nanoparticles with asymmetrically substituted tetraazamacrocycles is highly desired in biomedical applications of the magnetic/fluorescent nanocomposites in order to increase the stability of the nanocomposites in biological media. Hence, in this work we develop conjugates of asymmetric Tris{9(10),16(17),23(24)-4-(2-mercaptopyridine)-2-(4-carboxyphenoxy)phthalocyaninato}magnesium(II) (**MgPc**) or Tris{9(10),16(17),23(24)-4-(2-mercaptopyridine)-2-(4-carboxyphenoxy)phthalocyaninato}aluminum(III) chloride (**AlPc**), (Scheme 1) when conjugated to aminopropyltriethoxysilane functionalized $Fe_3O_4$ magnetic nanoparticles (**AIMN**) (conjugate). We explore the photophysical and photochemical parameters; and the PACT activity of these

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