



Synthesis and physicochemical properties of zinc and indium phthalocyanines conjugated to quantum dots, gold and magnetic nanoparticles



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ABSTRACT

This work reports on the conjugation of semiconductors quantum dots (QDs), gold (AuNPs) or Fe₃O₄ magnetic (MNPs) nanoparticles to 4-(4,6-diaminopyrimidin-2-ylthio) substituted indium or zinc phthalocyanines (Pcs). The QDs and MNPs were linked to the Pcs via an amide bond and by chemisorption onto AuNP surface. There is a general decrease in fluorescence quantum yields of the Pcs in the presence of all the nanoparticles. There is an increase triplet quantum yields for Pcs in the presence of AuNPs and QDs, but not in the presence of MNPs. AuNPs conjugates irrespective of the central atoms have the highest singlet oxygen quantum yield and are more photo-stable than all the other conjugates. MPCs are less photostable in the presence of MNPs.

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1. Introduction

Metallophthalocyanine (MPcs) have been extensively studied for applications such as in electrochemical sensors [1], Langmuir–Blodgett films [2], semi-conductors [3], liquid crystal [4], dye-sensitized cells (DSSC) [5] and photodynamic therapy (PDT) [6,7]. MPcs have been linked to nanoparticles such as a magnetic (MNPs) [8,9] and Au (AuNPs) [10,11] nanoparticles and quantum dots (QDs) [12,13] resulting in improvement in triplet state parameters which is fundamental to improved PDT activity. The improvement in triplet state parameters are as a result of the heavy atom effect of the nanoparticles (NPs) which encourages intersystem crossing (ISC) from the singlet to the triplet state of the MPc complex. In this work, we compare the effects of MNPs, AuNPs and QDs on the photophysical behaviour of InPc and ZnPc derivatives (complexes **2** and **3**, Scheme 1). Even though a number of MPc complexes have been linked to these NPs, studies using InPc derivatives are unknown with the exception of our recent report for optical limiting studies [14]. Due to the size of the In central metal, larger ISC is expected. We show in this work that ISC rates as high as 90% are obtained when an InPc derivative is employed in the

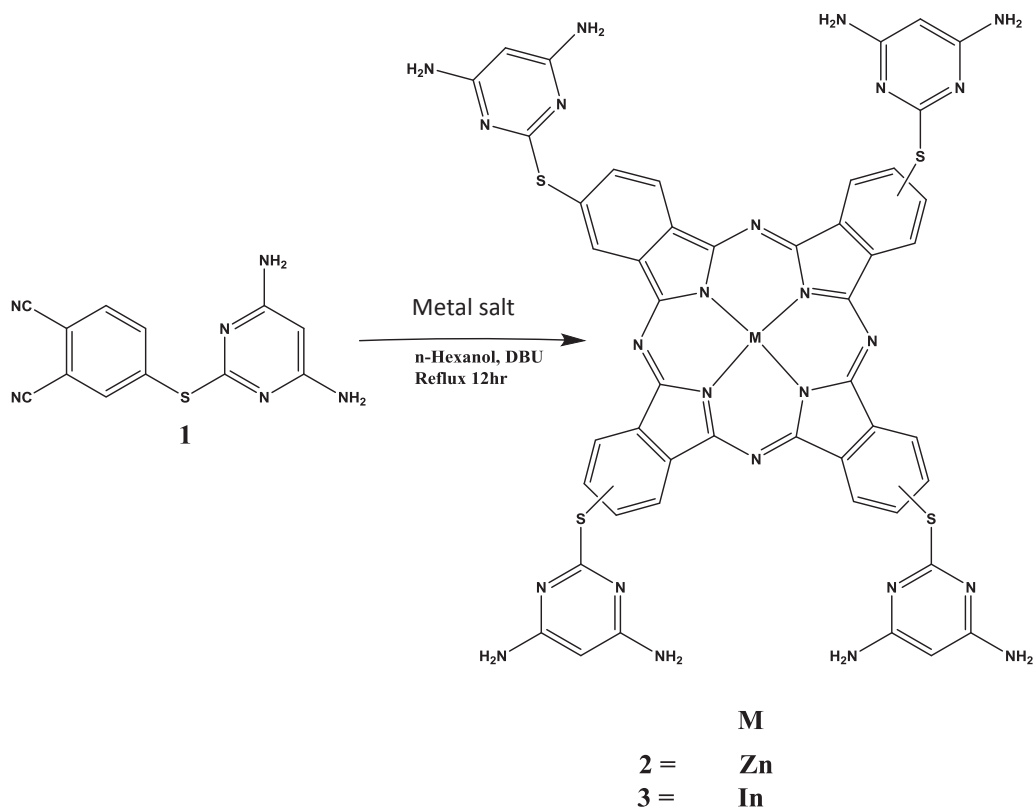
presence of the NPs.

QDs are inorganic semi-conductor fluorescent nanoparticles with a size range of 1–20 nm [15]. QDs are energy donors in the presence of acceptors [12,16]. QDs have found applications in many areas including in imaging [16–18] and photodynamic therapy (PDT) [19,20]. QDs and MPcs are both PDT agents and their combination may result in improvement in PDT. Also QDs may transfer energy to Pcs through Förster resonance energy transfer (FRET) [12,13]. FRET will be evaluated in this work. On the other hand, AuNPs have tuneable optical properties, which depend on the size, shape and capping agent [21–23]. AuNPs are known to enhance accumulation (into tissue) of photosensitizers [24], hence are of importance in this work. MNPs are nontoxic, biocompatible, injectable and have high-level accumulation in the target tissue or organ hence are suitable for medical applications [25]. Magnetic nanoparticles have potential for use in various fields such as magnetic resonance imaging (MRI), hyperthermia, drug delivery and cell separation [26–29]. The construction of hybrid nanoparticles containing phthalocyanines as photosensitizers in combination with quantum dots, magnetic or gold nanoparticles is aimed at developing nanosystems that have biomedical properties which are superior to the individual components.

This work describes the synthesis, photochemical and photophysical properties of 4-(4,6-diaminopyrimidin-2-ylthio) substituted indium or zinc phthalocyanines alone and when

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Scheme 1. Synthetic route of the metallophthalocyanines 2 and 3.

conjugated to different nanoparticles (Au, MNP-COOH or QD). The NH_2 group on the phthalocyanine will aid in the formation of an amide bond with QDs and MNPs. The quantum dots employed are core/shell/shell GSH capped CdTe/ZnSe/ZnO quantum dots, since core/shell/shell QDs have enhanced optical properties [30]. MNPs and QDs containing COOH groups were covalently linked to the amino group on the periphery of the phthalocyanines via amide bond linkage. Conjugation of the MPC was via chemisorption on the surface of the Au nanoparticles to form Au–S or Au–N due to affinity of Au to nitrogen and sulphur atoms [31–33].

2. Experimental

2.1. Materials

The following chemicals were obtained from Sigma–Aldrich: indium(III) chloride, zinc acetate dihydrate, absolute ethanol (EtOH), 1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC), N-hydroxysuccinimide (NHS), dicyclohexylcarbodiimide (DCC), toluene, spectroscopic dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), zinc phthalocyanine (ZnPc), Rhodamine 6G, 1,3-diphenylisobenzofuran (DPBF), 1,8-diazabicycloundec-7-ene (DBU), gold (III) chloride trihydrate, hexadecylamine (HDA) and sodium borohydride. Deuterated dimethyl sulfoxide (DMSO-d_6) was purchased from SAARCHEM, Ultra-pure water was obtained from a Milli-Q Water System (Millipore Corp, Bedford, MA, USA). Carboxylic acid functionalized magnetic nanoparticles (MNPs) [34], and glutathione (GSH) capped CdTe/ZnSe/ZnO quantum dots [30] were synthesized according to procedure reported earlier in our research group. 4-(4-(2-Diaminopyrimidin-2-ylthio)phthalonitrile (**1**) was synthesized as reported before [35].

2.2. Equipment

The absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Transmission electron microscopy (TEM) images were obtained using a ZEISS LIBRA[®] transmission electron microscope. Infrared (IR) spectra were collected on a Bruker Alpha model FT-IR spectrometer with platinum-ATR. Fluorescence emission spectra were recorded on a Varian Eclipse spectrofluorimeter.

Irradiations for singlet oxygen and photodegradation quantum yield determinations were performed using a General Electric Quartz lamp (300 W), 600 nm glass (Schott) and water filters were used to filter off ultra-violet and far infrared radiations respectively. An interference filter, 700 nm with a band of 40 nm, was placed in the light path just before the cell containing the sample. Light intensities were measured with a POWER MAX 5100 (Molelectron detector incorporated) power meter and were found to be 3.8×10^{16} photons $\text{cm}^{-2} \text{s}^{-1}$. Mass spectral data were collected with a Bruker AutoFLEX III Smartbeam TOF/TOF Mass spectrometer. The spectra were acquired using dithranol as the MALDI matrix. ^1H and ^{13}C nuclear magnetic resonance spectra were recorded on a Bruker AMX 600 MHz NMR spectrometer. X-ray Diffraction (XRD) analysis was performed on a Bruker D8 Discover diffractometer, equipped with a Lynx Eye detector, under $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). Data were collected in the range from $2\theta = 10^\circ$ to 100° , scanning at $0.010^\circ \text{ min}^{-1}$ and 192 s per step. The samples were placed on a zero background silicon wafer slide.

Fluorescence decay times were measured using a time correlated single photon counting (TCSPC) setup (FluoTime 300, 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).

Laser flash photolysis system was used for the determination of triplet decay kinetics. Details of the equipment have been provided

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