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Synthesis and singlet oxygen production by a phthalocyanine when embedded in asymmetric polymer membranes

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ABSTRACT

2(3),9(10),16(17),23(24)-Tetrakis-(4-aminophenoxy)phthalocyaninato indium (III) chloride (ClInTAPPc, **3**) was first conjugated to two different polymers: polystyrene (PS) and polyacrylonitrile (PAN) to form **3**-PS and **3**-PAN. The conjugates were cast into the corresponding polymers to form membranes represented as **3**-PS-membrane and **3**-PAN-membrane, respectively. The prepared membranes were characterized using various techniques including scanning electron microscopy and solid state UV/Vis spectroscopy. Singlet oxygen quantum yields were higher for the **3**-PS-membrane at 0.51 compared to **3**-PAN-membrane at 0.35. The larger singlet oxygen also applies to **3**-PS (0.63) compared to **3**-PAN (0.38) when in solution.

1. Introduction

Many methods and techniques used for water purification involve the physical separation of pollutants or contaminates and hence are relatively ineffective against most chemical pollutants [1–4]. One of the approaches for water purification has been to reduce the size of particles to be removed using nanoporous materials [1–4]. However such systems still prove limited when it comes to small molecule pollutants. Adsorption technology provides a good contribution towards solving this problem [5,6]. Due to limited reuse of adsorbents, adsorption technology may prove to be cost-ineffective. The materials for consideration must then be functionally effective, reusable and produced at relatively low cost.

Research on metallophthalocyanines (MPcs) and their analogues continues to grow due to their interesting optical properties which may be exploited for different applications [7,8]. These properties include efficient singlet oxygen generation, photostability and flexible structural modification [9–12]. These properties make Pcs potential photosensitizes for photodegradation of organic pollutants. In addition to these properties, Pcs have strong absorbance in the biological optical window region (600-800 nm) and many do not have dark toxicity [10–12], making them potential candidates for application in photodynamic therapy (PDT) and photodynamic antimicrobial therapy (PACT). The photoactivity properties of Pcs have resulted in the extension of their application to photocatalytic purification of water [13–17].

In this work, 2(3),9(10),16(17),23(24)-tetrakis-(4-aminophenoxy)phthalocyaninato indium (III) chloride (ClInTAPPc, **3**) was conjugated (via an amide bond) to COOH substituted polyacrylonitrile (PAN, **2A**) and polystyrene (PS, **2B**) polymers (Schemes 1 and 2), to form **3**-PAN and **3**-PS, respectively. **3**-PAN and **3**-PS were further embedded (through casting) in corresponding pristine PAN (**1A**) and unfunctionalized PS (different from functionalized **1B** or **2B** in Scheme 1) polymers to form membranes represented as **3**-PAN-membrane and **3**-PS-membrane. The choice of the unfunctionalized polymers for casting was based on availability and ease of casting as will be discussed below. In preliminary experiments, we observed leaching of the Pc from the membrane when the Pc was simply mixed with the polymer solution (without prior conjugation) before membrane casting. Hence, the Pc was covalently linked to each polymer to form **3**-PAN and **3**-PS, before the formation of the membranes (represented as **3**-PAN-membrane and **3**-PS-membrane) in this work. This is the first time that Pcs are embedded in polymer membranes. The membranes employed in this work are termed asymmetrical due to the method of synthesis which results in an asymmetrical cross-section (the membranes consist of bulk and thin skin). In earlier work we have embedded phthalocyanines in electrospun fibres, with the phthalocyanines

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