



Photophysical and photochemical properties of Ni(II), Pd(II) and Pt(II) aryloxo and alkylthio derivatised phthalocyanine

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ABSTRACT

Several aryloxo (**3a–6a** and **3b–6b**) and alkylthio (**3d** and **3e**) derivatised phthalocyanines were synthesized, characterized and the photochemical and photophysical properties investigated along with those of the previously reported (**3c–5c**, **4d**, **5d**, **4e** and **5e**) complexes. The effects of open-shell metals (Ni(II), Pd(II) and Pt(II)) on the photophysical and photochemical properties of the phthalocyanine ligands were investigated. Palladium and platinum improved the triplet quantum yield and singlet oxygen generation capacities of the unmetalated phthalocyanines (**3a–3e**) making their complexes candidates for further investigation in photocatalysis. Ni(II)Pc analogues gave poor results compared with their Pd(II)Pc and Pt(II)Pc counterparts.

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1. Introduction

Metallophthalocyanine (MPc) complexes containing diamagnetic central metals are well known as photosensitizers in photodynamic therapy [1,2]. This is due to their ability to efficiently produce singlet oxygen [1], which mediates photosensitized reactions of MPc complexes. Generally, diamagnetic metals promote intersystem crossing (ISC), producing long lived triplet excited states [3–9].

Because of considerable d– π interactions which quench the excited states, short triplet state lifetimes (τ_T) are observed for open-shell MPc complexes. In spite of this theoretical shortcoming PdPcs are being investigated in the areas of photocatalysis [10,11] because of their high photostability. The short triplet state lifetimes implies that MPc complexes decay from the electronically excited state to the ground state primarily by non-radiative pathways, releasing their energy in several forms, including heat. Thus the possibility exists of producing local photosensitized hyperthermal effects with open shell phthalocyanines leading to specific damage of the cells and tissues containing the photosensitizer, without affecting healthy tissues [12]. This is the basis for photothermal therapy (PTT) of cancer, and nickel octabutylxynaphthalocyanine and nickel octabutylxynaphthalocyanine have gained a lot of attention in this area [13]. Thus, systematic investigation of the photophysical properties of MPcs containing open-shell metals,

especially Ni(II), Pd(II) and Pt(II) is essential for possible applications, such as in PTT. Such studies are scarce in the literature for these MPc complexes.

This work reports on the syntheses, and photophysical and photochemical characterization of metal-free, Ni, Pd and Pt phenoxy (**3a–6a**) and benzyloxyphenoxy (**3b–6b**) phthalocyanine complexes. The syntheses of unmetalated alkylthio derivatives (**3d**, **3e**) are also reported. The choice of substituents (**a**) (phenoxy) and (**b**) (benzyloxyphenoxy) is based on our previous study of these substituents on MPc complexes containing other central metals (e.g. OTi(IV), ClIn(IV), ClGa(IV), Cd and Pb) where these ligands were found to prevent aggregation in some cases, hence enhancing photochemical and photophysical behavior of the MPc complexes [14–18]. NiPc complexes in particular are known to be highly aggregated even when bulky ligands are employed [19].

The effects of substituents and central metals on the photochemical and photophysical properties for **3a–6a**, **3b–6b** and **3d**, **3e** are compared with those of previously reported pentylthio, octylthio and dodecylthio substituted NiPc (**4c–4e**) and PdPc (**5c–5e**) derivatives and unmetalated pentylthio Pc (**3c**) [20,21].

2. Experimental

2.1. Materials

Nickel chloride hexahydrate, palladium chloride and platinum chloride, potassium carbonate, 8-diazabicyclo[5.4.0]undec-7-ene (DBU), diphenylisobenzofuran (DPBF), and phenol were purchased

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