



Synthesis and photophysical properties of octa-substituted phthalocyaninato oxotitanium(IV) derivatives

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ABSTRACT: The synthesis, spectral and photophysical properties including fluorescence quenching of the following octa-substituted oxotitanium phthalocyanines are reported: 2,3,9,10,16,17,23,24-octaphenoxypthalocyaninato titanium(IV) oxide, 2,3,9,10,16,17,23,24-[octakis(4-*t*-butylphenoxyphthalocyaninato)]titanium(IV) oxide, 2,3,9,10,16,17,23,24-[octakis(4-benzyloxyphenoxyphthalocyaninato)]titanium(IV) oxide and 2,3,9,10,16,17,23,24-octaphenylthiophthalocyaninato titanium(IV) oxide. The complexes are characterized by ¹H NMR, IR and UV-vis spectroscopies. Their photophysical properties are presented where moderate fluorescence quantum yields (0.14-0.19) and lifetimes were determined. Varied triplet quantum yields were obtained and the triplet lifetimes (40-100 μs) were short. Copyright © 2006 Society of Porphyrins & Phthalocyanines.

KEYWORDS: titanium, phthalocyanines, substitution, quantum yields, quenching.

INTRODUCTION

Phthalocyanines (Pcs) are 18 π electron systems which have continuously been the subject of research for over seven decades due to their unique properties. Their unique stability and electronic features, together with their broad versatility have found wide applications in fields such as liquid crystals [1], chemical sensors [2], non-linear optics [3-5], photodynamic therapy [6, 7] and catalysis [8]. For such applications, solubility is a prerequisite as this facilitates their characterization. To increase the solubility of these macrocycles, appropriate substituents are introduced at the periphery of the ring. It can thus be envisaged that the presence of these substituents alters the intrinsic properties of the molecule since they alter the electronic distribution of the Pc ring [9]. In this way, the bulk characteristic of the molecule may be tailored. With substitution, new materials which may show improved or more

functional characteristics may also be developed. For example, a large network of conjugated π electrons confers a high electrical polarizability to the ring, thus offering the possibility of several kinds of electronic transitions in the UV-vis spectral range [10].

Phthalocyanine structural modifications such as the substitution of donor-acceptor groups on the ring and the heavy atom effect tend to vary the excited state properties in these molecules. There is an intrinsic curiosity about how Pcs can be made and in understanding the properties of their low-lying electronic states. In addition, the potential which some of the Pcs have for use as near-infrared light absorbers in optical data storage is immense.

Due to an electron transfer, phthalocyanine fluorescence can be strongly quenched by an electron acceptor. Quenching by quinones, *e.g.* benzoquinone (BQ) and hydroquinone (HQ), is of utmost interest due to the important role of the quinone moiety as an electron acceptor in photobiological processes [11]. Titanium based phthalocyanines have been reported [12-15] but their photophysics is rare compared to the consistent investigations of other first-row, transition metal phthalocyanines.

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