

Synthesis, Photophysical and Photochemical Properties of Poly(oxyethylene)-Substituted Phthalocyaninato Oxotitanium(IV) Complexes

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The synthesis, photophysical and photochemical properties of tetra- and chlorotetrapoly(oxyethylene)-substituted oxotitanium(IV) phthalocyanines are reported for the first time. The new compounds were characterized by elemental analysis, IR, ¹H and ¹³C NMR spectroscopy, electronic spectroscopy and mass spectra. These complexes showed monomeric behaviour in solution. General trends are described for photodegradation, singlet oxygen, triplet state and fluorescence quantum yields, and triplet and fluorescence lifetimes of these compounds in dimethyl sulfoxide (DMSO). Photophysical and photochemical properties of phthalocyanine complexes are very useful for PDT applications. The com-

plexes showed high triplet quantum yields and triplet lifetimes in DMSO. The singlet oxygen quantum yields (Φ_{Δ}), which give an indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (Type II mechanism), were 0.72 and 0.78 for **3a** and **5a**, respectively. Thus, these complexes show potential as Type II photosensitizers. These complexes were also quenched by benzoquinone for fluorescence quenching studies.

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Introduction

Recently, phthalocyanine (Pc) chemistry has undergone a renaissance because these compounds and many of their derivatives exhibit properties that are interesting for many applications in material science.^[1,2] Current research on phthalocyanines (Pcs) has been rapidly expanding into several applied fields including photovoltaics, electrochromism, optical data storage, laser dyes, liquid crystals, chemical sensors and photosensitizers for photodynamic therapy.^[3] Because of their properties as semiconductors as well as their large linear and nonlinear optical responses, Pcs are currently of great scientific and technological interest for designing novel electronic and photonic devices. Pcs with highly delocalized cyclic π -electron systems show intense absorptions in the red region (Q band) and these absorptions can be shifted to the near IR region by making relatively small changes in these molecules.^[3,4] Fusion of additional aromatic rings (polybenzannulation) has been proposed as a practical method to enhance the conjugation of π -electrons, thus increasing the wavelength of absorbed electromagnetic radiation. However, there is a decrease in the solubility of the products obtained by increased conjugation.^[5] The second way to obtain the same effect has been

the addition of electron donating groups (e.g. -OR, -SR, etc.) into the periphery of Pcs.^[1] The presence of substituents is an additional advantage, as they address the problem of insolubility by making the complexes soluble in most organic solvents as opposed to unsubstituted Pcs that have limited applications. Tetra-substituted Pcs are usually more soluble than the corresponding octa-substituted Pcs due to the formation of constitutional isomers and the high dipole moment that results from the unsymmetrical arrangement of the substituents at the periphery.^[6–9] The other method for changing the absorption wavelength is the use of some special metals in the inner core, and TiO²⁺ is one of them.^[10] Unsubstituted oxotitanium phthalocyanine (OTiPc), a well-known near-IR-active photoconductive dye used as xerographic photoreceptor in copiers and laser printers,^[11–13] was first synthesised by Taube.^[14] Also, this material can be used in optical disc information recording. The high third order optical susceptibility values of OTiPc derivatives are well documented.^[15] Specific phthalocyanines can thus be tailored such that they consist of certain properties that are required for various applications since the possibility of combining an unlimited number and type of substituents with a great number of central metals is infinite.

Thiol-derivatized metallophthalocyanine complexes show rich spectroscopic and photochemical properties. For example, they are known to absorb at longer wavelengths^[16–21] than other metallo phthalocyanine complexes. To the best of our knowledge, titanium phthalocyanines

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