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Spectroscopic characterisation and interactions of sulfonated titanium and tantalum phthalocyanines with methyl viologen

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Abstract

Sulfonated OTiPc(S)$_n$ and (Cl$_3$)TaPc(S)$_n$ complexes are prepared and characterised by spectroscopic methods in DMSO, methanol and PBS 7.4. The dominant sulfonated species was the disulfophthalocyanine. OTiPc(S)$_n$ is highly aggregated in PBS 7.4 solution and tends to partially monomerise, on addition of Triton X-100, while (Cl$_3$)TaPc(S)$_n$ showed broadened spectra in all solvents and was not affected by Triton X-100. The absorption and excitation spectra of OTiPc(S)$_n$ are similar and are mirror images of their emission spectra in DMSO, but differ in PBS and methanol. The fluorescence quantum yields (ϕ_F) and lifetimes (τ_F) were larger in DMSO than in methanol. In PBS 7.4, however, the ϕ_F and τ_F values were significantly smaller for OTiPc(S)$_n$, which is typical of aggregated species. Gradual addition of the electron-acceptor MV^{2+} to solutions of MPc(S)$_n$ complexes resulted in the fluorescence quenching of complexes with higher quenching observed for OTiPc(S)$_n$. The interaction of the MPc(S)$_n$ complexes with MV^{2+}, and hence the stoichiometry and association constants are evaluated by means of Job method.

Keywords: Phthalocyanines; Titanium; Tantalum; Methyl viologen; Spectrophotometry; Quenching

1. Introduction

Tetrapyrrole macrocycles such as porphyrins and phthalocyanines can be grafted with ionic substituents of opposite charges in order to form stable ion-pairs. These individual components are held together by the coulombic attraction between the charged substituents and the hydrophobic interaction of the aromatic macrocycles. In most cases, the properties of the mixed complexes may notably differ from those of the parent compounds. The mixed complexes may display different and complementary absorption spectra, thus spectroscopic methods can be used to study their properties. The stoichiometry of the mixed complexes is commonly determined by Job's method which has been successfully used for tetrapyrrole systems [1–3]. Ion-pairs have been used in photoelectrochemical cells [4,5] as well as the photo-reduction of water [6,7] to hydrogen.

Complexation plays an important role in catalysis, genetic information, enzyme–substrate interactions and many other important processes. Biological processes such as photosynthesis and oxidative processes that involve the degradation of biological material in living cells, show an important role that the ion-pairs, and hence electron-transfer reactions, play in such systems [8]. Phthalocyanines (Pcs) are in fact extensively used in photodynamic therapy (PDT) of cancer where electron-transfer reactions occurring in living cells take place [9]. Electronically charged phthalocyanines such as sulfonated phthalocyanines have potential use as water-soluble electron-transfer photosensitisers, in for example photo-reduction of water to hydrogen, when used in conjunction with electron-acceptor molecules [10,11] such as methyl viologen. The focus has been more on the most pronounced complexation of cationic molecules such as viologens with anionic porphyrins [12–14]. The interest in studying electron-transfer reactions

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