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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.
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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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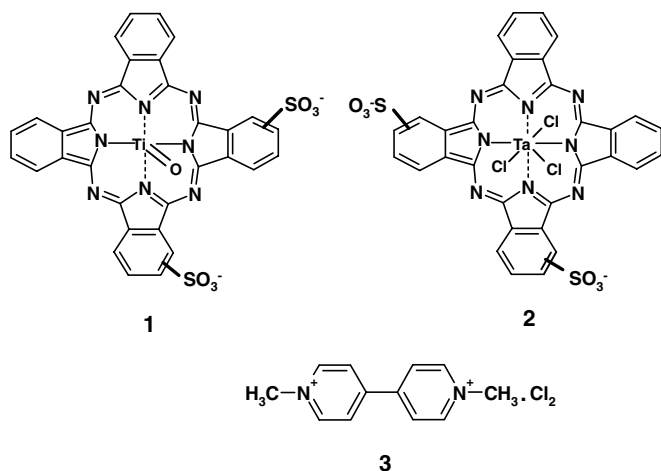Fig. 1. Molecular structures of sulfonated metallophthalocyanines OTiPc(S)$_n$ (**1**), (Cl$_3$)TaPc(S)$_n$ (**2**) and methyl viologen (**3**, MV^{2+}).

within pairs of phthalocyanines and methyl viologens has thus prompted us to spectroscopically characterise reactions within pairs formed by methyl viologen (MV^{2+}, **3**) with sulfonated titanium (**1**) and tantalum phthalocyanines (**2**), abbreviated as OTiPc(S)$_n$ and (Cl$_3$)TaPc(S)$_n$, Fig. 1. The choice of TaPc complexes is based on the fact that the central Ta metal is large (and a d^0) and will enhance intersystem crossing to the the triplet state, hence increase the yield of the triplet state. TiPc containing a d^0 metal, will also have enhanced triplet yields. Both of these metal pthalocyanines have potential as photocatalysts but their properties have not been explored compared to other closed shell MPcs such as ZnPc. In this work, the spectroscopic and fluorescence properties of the sulfonated OTiPc and (Cl$_3$)TaPc complexes are presented. Their interactions with MV^{2+} are investigated and the existence of MPc(S)$_n$–MV^{2+} heteroaggregates is demonstrated by UV–Vis spectroscopy.

2. Experimental

2.1. Materials and reagents

Sulfonated phthalocyanines, namely OTiPc(S)$_n$ and (Cl$_3$)TaPc(S)$_n$ were synthesised from (O)TiPc [15] and (Cl$_3$)TaPc [16,17], respectively, using oleum (30%, SO$_3$) according to a literature method described for MPc(S)$_n$ [18–20]. The complexes were characterized by UV–Vis and IR spectroscopies and by high-performance liquid chromatography (HPLC). Methyl viologen dichloride hydrate and Triton X-100 were obtained from Aldrich. Methanol, dimethyl sulfoxide (DMSO) and phosphate buffer solution (PBS, pH 7.4) were used as solvents.

2.2. Equipment

UV–Vis spectra were recorded on a Cary 500 UV–Vis/NIR (near infrared) spectrophotometer. Fluorescence exci-

tation and emission spectra were recorded on a Varian Eclipse spectrofluorometer. High-performance liquid chromatography (HPLC) was performed on Quad-Gradient HPLC system, Agilent 1100 Series; fitted with an analytical column, General Phenomenex C18 LUNA and connected to a variable UV–Vis detector (set at $\lambda = 330$ nm). The mobile phase comprised of 50:50 methanol:water mixture, with a flow rate of 1 ml min^{-1} and sample injection volume of 20 μl. IR spectra (KBr pellets or using Nujol) were recorded on a Perkin–Elmer spectrum 2000 FTIR spectrometer.

2.3. Methods

2.3.1. Interaction studies between MV^{2+} and $MPc(S)_n$

The interaction between MPc(S)$_n$ and MV^{2+} was studied spectrophotometrically, by gradual addition of small aliquots (typically 5 μl) of 10^{-3} M solution of MV^{2+} to 5 ml of 10^{-5} M solution of MPc(S)$_n$. The added volumes were taken into account in the construction of Job diagrams. Spectroscopic measurements were performed at room temperature in 1 cm quartz cells.

2.3.2. Fluorescence quantum yields

The fluorescence quantum yields (ϕ_F) were determined by the comparative method (Eq. (1)) [21,22]:

$$\phi_F = \phi_{F(Std)} \frac{F \cdot A_{Std} \cdot \eta^2}{F_{Std} \cdot A \cdot \eta_{Std}^2} \qquad (1)$$

where F and F_{Std} are the areas under the fluorescence curves of the MPc(S)$_n$ and the standard, respectively, A and A_{Std} are the respective absorbances ($\sim$0.05) of the sample and standard at the excitation wavelengths, and η^2 and η_{Std}^2 are the refractive indices of solvents used for the sample and standard, respectively. Chlorophyll *a* in ether ($\phi_F = 0.32$) [23], was employed as the standard.

2.3.3. Fluorescence lifetimes and natural lifetime calculations

Theoretically, the natural or radiative lifetimes, τ_N, are related to the absorption band area. Using the absorbance and fluorescence spectra, natural lifetimes were estimated using Eq. (2) [24–26]:

$$\frac{1}{\tau_N} = 2.88 \times 10^{-9} \eta^2 \frac{\int \frac{F(\lambda)}{\lambda^2} \cdot d(\lambda)}{\int F(\lambda)\lambda \cdot d(\lambda)} \int \frac{\varepsilon(\lambda)}{\lambda} \cdot d(\lambda) \qquad (2)$$

where η is the refractive index of the solvent, $F(\lambda)$ and $\varepsilon(\lambda)$ are the areas under the fluorescence and absorption spectra, respectively. ORIGINPRO 7.5 software was employed for the calculations using Eq. (2). The fluorescence lifetimes τ_F were evaluated using the following equation:

$$\phi_F = \frac{\tau_F}{\tau_N} \qquad (3)$$

2.3.4. Fluorescence quenching by methyl viologen (MV^{2+})

Fluorescence quenching experiments were carried out by addition of increasing concentrations of the quencher,