



Synthesis, photophysical and photochemical properties of octa-substituted antimony phthalocyanines

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ABSTRACT

This work reports on the synthesis and photophysical parameters of unsubstituted $[\text{Sb}^{\text{III}}\text{Pc}]^+\text{I}_3^-$ and octa-phenoxy ($[\text{Sb}^{\text{III}}\text{OPPC}]^+\text{I}_3^-$) and -4-*t*-butylphenoxy ($[\text{Sb}^{\text{III}}\text{OTBPPC}]^+\text{I}_3^-$) substituted antimony phthalocyanines. Photophysical and photochemical properties were studied for these complexes in dimethylsulfoxide, dimethylformamide and toluene. The excitation spectra of oxidized antimony (Sb(V)Pc) derivatives were similar to absorption spectra. Low fluorescence quantum yields, high triplet quantum yields and low triplet lifetimes were observed as the result of heavy atom (antimony ion).

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1. Introduction

Since their accidental discovery in the early 1900s, metallophthalocyanines (MPcs) have attracted much interest [1] due to their high chemical and thermal stability, high degree of aromaticity, synthetic flexibility and ability to adapt to a wide range of applications, including in non-linear optics [2,3] and photodynamic therapy [4].

MPcs exhibit intense absorption towards the red end of the visible spectrum, and the wavelength varies depending on the central metal and the type, number and position of substituents attached to the phthalocyanine macrocycle [5]. The presence of substituents on the Pc ring increases the solubility and also reduces molecular aggregation. Some central metal ions can allow axial ligation, which increases solubility, reduces molecular aggregation and brings about changes to the electronic structure of the molecule due to the dipole moment of the central metal-axial ligand bond [6]. MPcs containing heavy atoms such as antimony are expected to show enhanced intersystem crossing [7], resulting in improved photophysical and photochemical properties.

There has been less attention paid to MPc derivatives of group-15 elements except for a few reports on antimony and bismuth complexes of phthalocyanine [8–14]. Some properties of SbPc derivatives show distinct differences compared to the majority of MPc complexes. For example, the Sb tetra-*tert*-butyl phthalocyanine $[\text{SbTBPC}]_3$ has shown the formation of J aggregates (red-shifted) in non-aqueous solutions [12]. J aggregates are rare in

non-aqueous media for MPc complexes. The $[\text{SbTBPC}]_3$ complex was found to be stable in the dark in chloroform and dichloromethane, but readily demetalated in donor solvents such as dimethylformamide (DMF) and tetrahydrofuran (THF) [15]. Photobleaching of this complex occurred under visible light irradiation in chloroform. Attempts to determine singlet oxygen producing ability of $[\text{SbTBPC}]_3$ using 1,3-diphenylisobenzofuran (DPBF) as a quencher resulted in oxidation of Sb(III) to Sb(V) [15]. It has also been reported that some SbPc complexes do not show fluorescence in the Q-band region [12,15]. However, the behaviour of the triplet state of SbPc complexes has not been explored. Hence, in this work we report on the synthesis of new SbPc complexes: octa-phenoxy ($[\text{Sb}^{\text{III}}\text{OPPC}]^+\text{I}_3^-$) and -4-*t*-butylphenoxy ($[\text{Sb}^{\text{III}}\text{OTBPPC}]^+\text{I}_3^-$) substituted antimony phthalocyanines and on their photophysical and photochemical behaviour.

2. Experimental

2.1. Materials

Acetone, ethanol, chloroform (CHCl_3), methanol (MeOH), 1-chloronaphthalene (1-CNP), 1-octanol, tetrahydrofuran (THF), dimethylformamide (DMF), hexane and deuterated chloroform (CDCl_3) were obtained commercially and dried before use. Potassium carbonate (K_2CO_3), urea, phenol, 4-*tert*-butylphenol and phthalonitrile were purchased from Aldrich and used as received. Dimethylsulphoxide (DMSO) was purchased from SAARCHEM, and dried in alumina before use. 4,5-Dichlorophthalonitrile (**3**) [16] was synthesized and purified according to literature procedure.

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