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Synthesis, photophysical and nonlinear optical properties of microwave synthesized 4-tetra and octa-substituted lead phthalocyanines

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ABSTRACT

This work presents the photophysical and nonlinear optical behaviour of newly synthesized complexes: 2,(3)-tetrakis(4-benzyloxyphenoxyphthalocyaninato) lead (**5a**) and 2,3-octakis(4-benzyloxyphenoxyphthalocyaninato) lead (**6a**). The nonlinear optical behaviour of complexes **5a** and **6a** are compared with those of 2,(3)-tetraphenoxyphthalocyaninato lead (**5b**), 2,(3)-tetrakis(4-t-butylphenoxyphthalocyaninato) lead (**5c**), 2,3-octaphenoxyphthalocyaninato lead (**6b**) and 2,3-octakis(4-t-butylphenoxyphthalocyaninato) lead (**6c**). The synthesis of **5a** and **6a** was performed using microwave irradiation. Photophysical properties were studied for these complexes in dimethylsulfoxide, dimethylformamide, toluene, tetrahydrofuran and chloroform. The fluorescence spectra were different from excitation spectra due to demetallation upon excitation. High triplet quantum yields ranging from 0.80 to 0.86 (in DMSO, DMF and toluene) and low triplet lifetimes (20–50 μs in DMSO, and <10 μs in the rest of the solvents) were observed due to the presence of heavy atom. Nonlinear optical properties were studied in dimethylsulfoxide. The optical limiting threshold intensity (I_{lim}) for the PbPc derivatives were calculated and ranged from 2.1 to 6.6 W/cm^2.

1. Introduction

Since the discovery and invention of intense light sources based on laser mechanisms in the 1960s [1], the need for development of protective devices against laser radiation has motivated substantial research in this field of study [2].

Nonlinear optics (NLO) is a branch of optics that is associated with the changes in the optical properties of material when it interacts with light [3]. Several optical technologies such as optical rectifiers, optical switches, dynamic holography, optical data-recording and optical limiters are based on nonlinear effects [4].

When interference light interacts with light-sensitive material or elements, damage may occur if a protective devise is not available. This is where optical limiting becomes crucial; in the protection of light-sensitive elements such as optical sensors, human eyes and other light-sensitive material.

Among NLO materials, metallophthalocyanines (MPcs) are of great interest because they have several advantages over inorganic materials currently in use for optical limiting. The advantages include: fast response times (subpicosecond) [5], small dielectric constants [4] and ease of fabrication and processing.

MPcs have low solubility in most organic solvents and they readily aggregate. Central metals play a major role in tuning the properties of MPcs, some central metal ions can allow axial ligation, which increases solubility and reduces molecular aggregation [6]. The solubility can also be increased by introducing alkyl or alkoxy groups in the peripheral or non-peripheral position of Pc framework [7].

Heavy metals such as lead play a major role in optical limiting mechanisms since they enhance intersystem crossing through spin orbit coupling. PbPc derivatives have been shown to give good optical limiting properties [8–11] when compared to NiPc and H_2Pc, however PbPc derivatives are readily demetallated upon excitation [9,12].

In this work we report on the microwave synthesis of PbPc derivatives tetra (**5a**)- and octa (**6a**)-substituted at peripheral positions with 4-benzyloxyphenoxy groups. The photophysical (triplet state lifetimes and quantum yields, and fluorescence quantum yields) and nonlinear optical parameters of **5a** and **6a** complexes are presented. The NLO parameters of these complexes are compared to those of **5b**, **5c**, **6b** and **6c**, whose syntheses and photophysics have been reported [12].

2. Experimental

2.1. Materials

Chloroform ($CHCl_3$), methanol (MeOH), 1-octanol, tetrahydrofuran (THF), dimethylformamide (DMF), toluene and hexane were

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