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Spectroscopic and nonlinear optical properties of alkyl thio substituted binuclear phthalocyanines

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ABSTRACT

This work presents the spectroscopic and nonlinear optical properties of metal free binuclear and monomeric 4-(pentylthio)phthalocyanine and cobalt 4,5-(bipentylthio)phthalocyanine. Second order nonlinear absorption coefficient (β) values for the complexes were determined and compared.

1. Introduction

It is known that the absorbance of materials with reversible saturable absorption (RSA) characteristics increase when irradiated with strong laser light [1]. The above property of the material has made possible important applications of these materials, such as optical limiters for protecting electro-optical sensors from high intensity light [2–5]. Generally RSA is observed under high intensity light, as it is deemed necessary for populating the excited state. Population of the excited state would result in the excited state having higher extinction coefficient with respect to the ground sate, thus leading to RSA occurrence [6]. Materials such as metallophthalocyanines (MPcs) have received considerable attention due to their strong nonlinear optical properties [7,8]. To date MPcs have consistently shown RSA to occur at high intensity laser light. The connection between molecular structure and NLO activity, especially for third order NLO properties is not well understood. Amongst many factors it is known that increasing dimensionality and π-delocalisation possibilities can result in increasing third order nonlinearity [7,9,10]. The involvement of ligand-to-metal charge-transfer transition in organometallic complexes, and increasing electron accepting ability of the metal are important factors contributing to enhanced nonlinear optical properties of organometallic complexes [11]. Dimers of centrosymmetric squaraine molecules have also been shown to improve second harmonic generation (SHG) signal, which is a second order nonlinear effect. This behaviour was not expected and was named “heresy in the world of organic nonlinear optics” by Meyers et al. [12].

In this work we report nonlinear optical properties of binuclear cobalt 4-(pentylthio)phthalocyanine and binuclear cobalt 4,5-(pentylthio)phthalocyanine. The work comparatively studies the binuclear phthalocyanines (BiPcs) second order nonlinear absorption coefficient (β) with respect to monomeric Pcs using Z-scan.

2. Experimental

2.1. Material

1-Octanol, 1, 2- dichlorobenzene, *N,N*-dimethylformamide (DMF), Pentane thiol, Dihydroxybiphenyl, Potassium carbonate, Sodium chloride, Lithium metal and column chromatography silica were purchased from Sigma Aldrich. Tetrahydrofuran (THF), hexane, chloroform and hydrochloric acid (HCl) were obtained from SAARCHEM. Metalated and Metal-free 4-β-pentylthio phthalocyanine (Pc1), 4-β-pentylthio binuclear phthalocyanine (BiPc1), 4, 5-β-pentylthio phthalocyanine (Pc2) and 4, 5-β-pentylthio binuclear phthalocyanine (BiPc2) where synthesised and characterised following recently reported literature method [13] by the group (see Scheme 1 and SP).

2.2. Instrumentation

Ground state absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Magnetic circular dichroism (MCD) spectra were measured on a Chirasan Plus spectropolarimeter. Excitation spectra, emission spectra, fluorescence lifetimes and rotational lifetimes were measured with a Floutime 300 EasyTau spectrometer (PicoQuant GmbH). Mass spectral data were collected on a Bruker Auto FLEX (III) smart-beam MALDI- TOF mass spectrometer using Dithranol as the matrix in positive ion mode. All Z-scan experiments done in this work were performed using a frequency-doubled Nd: YAG laser (Quanta-Ray, 1.5 J/10 ns fwhm pulse duration) as the excitation source. The experimental details were as previously reported [8,14].

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