

Synthesis and photophysical properties of lead phthalocyanines

Desmond Kwena Modibane, Tebello Nyokong*

Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

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Abstract

This work reports on the synthesis and photophysical parameters of tetra- and octa-substituted new lead phthalocyanines. The complexes synthesized are: 1,4-(tetraphenoxyphthalocyaninato)lead (**7a**), 1,4-(tetra-*tert*-butylphenoxyphthalocyaninato)lead (**7b**), 2,3-(tetraphenoxyphthalocyaninato)lead (**8a**), 2,3-(tetra-*tert*-butylphenoxyphthalocyaninato)lead (**8b**), 2,3-octaphenoxyphthalocyaninatolead (**9a**), 2,3-[octakis(4-*t*-butylphenoxyphthalocyaninato)]lead (**9b**). Photophysical properties were studied for these complexes in a 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 0.70 to 0.88 (in DMSO, DMF and toluene) and low triplet lifetimes (20–50 μ s in DMSO, and <10 μ s in the rest of the solvents) were observed due to the presence of heavy atom.
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1. Introduction

Metallophthalocyanines (MPcs) have been investigated in detail for many years [1] because of their wide range of applications in many fields, including in chemical sensors [2], liquid crystals [3,4], Langmuir–Blodgett films [5], non-linear optics [6,7], optical data storage [8,9], various catalytic processes [10] and as carrier generation materials in near-IR devices [11]. For non-linear optical applications, MPcs have advantages over inorganic compounds currently in use due to their good conductivity [12], ease of processibility into optical components and their economic feasibility [7,12].

Central metals play a critical role in tuning the properties of MPcs [12]. 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 [13]. The coordination of the Pc ligand with metal will result in the alteration of

molecular conformation and several conformations are known [14]. The most common conformations are planar, ruffled, waved, domed, and skew domed. Pcs metallated with Pb or Sn show the domed conformation [15]. The essentially planar conformation of Pcs can also be distorted by substituents through conformational stress [16].

MPcs have low solubility in most organic solvents and they aggregate. The solubility can be increased by introducing alkyl or alkoxy groups into the peripheral and non-peripheral positions of the phthalocyanine framework [17]. Tetra-substituted Pc's show better solubility than the corresponding octa-substituted phthalocyanines due to the formation of constitutional isomers and the high dipole moment that results from the unsymmetrical arrangement of the substituents at the periphery [18,19]. Substitution at the more sterically crowded α (non-peripheral) causes red shifting of the Q-band and reduces aggregation tendencies more than substitution at β (peripheral) position [20].

Heavy metals, especially diamagnetic metals, play a major role in photosensitising and optical limiting mechanisms since central metals enhance intersystem crossing. Octa- and tetra-substituted PbPc derivatives have attracted attention in recent years [21–27]. Lead ion (Pb^{2+}) is unable

* Corresponding author. Tel.: +27 46 603 8260; fax: +27 46 622 5109.
E-mail address: t.nyokong@ru.ac.za (T. Nyokong).