



Photophysical characterization of dysprosium, erbium and lutetium phthalocyanines tetrasubstituted with phenoxy groups at non-peripheral positions

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ARTICLE INFO

Article history:

Received 20 October 2010

Accepted 18 March 2011

Available online 24 March 2011

Keywords:

Lanthanide ion

Phenoxy-substituted phthalocyanine

Photophysical and photochemical properties

ABSTRACT

Dysprosium bis-phthalocyanine and monomeric phthalocyanines of erbium and lutetium with non-peripheral phenoxy substituents have been synthesized using two different preparative routes. Photophysical studies on these phthalocyanines revealed that the triplet states of dysprosium and erbium are not populated while the monomeric phthalocyanine complex of lutetium is populated with a quantum yield of 0.83 and a lifetime of 25 μ s in DMSO. It was further found that the phthalocyanine complex of lutetium was capable of photochemical generation of singlet state molecular oxygen with yield of 0.71 in THF, thus a promising photosensitizer. However, the three phthalocyanine molecules have very low fluorescence quantum yields of less than 0.01.

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1. Introduction

In recent years, compounds of lanthanide ions (Ln^{3+}) with organic ligands have found wide application in areas such as fluorescence materials [1,2], electroluminescence [3], and as fluorescence probes and labels in a variety of biological systems [4–6]. Phthalocyanines (Pcs) are remarkable macrocyclic compounds that possess interesting physical and chemical properties [7–9]. Thus synthesis and characterization of novel phthalocyanine metal complexes, including those of the lanthanides continue to attract the attention of many researchers. Interest in lanthanide phthalocyanine complexes in particular, has been as a result of possible coordination of two or more phthalocyanine macrocyclic units per metal atom forming LnPc_2 , or Ln_2Pc_3 [10–13]. These lanthanide phthalocyanine derivatives have high intrinsic conductivity and interesting electrochemical and electrochromic properties [14].

The lanthanide phthalocyanine complexes obtained by conventional chemical methods usually contain one or two macrocycles per metal atom [10]. The type (whether monomeric or oligomeric) and amounts of the particular derivative in a reaction mixture depend on the ratio of starting metal salt to phthalonitrile as well as other reaction conditions [11,12]. Phthalonitrile: metal salt ratio of 6:1 or larger results in oligomeric derivatives, whereas 4:1 or smaller results in monomeric complexes [11–13]. Thus oligomeric forms of phthalocyanine complexes of lanthanides can be obtained if the initial phthalonitrile content is high.

Apart from the initial phthalonitrile:metal ratio in deciding the nature of the lanthanide phthalocyanine complex, it has also been established that the particular lanthanide metal also determines

the type of phthalocyanine complex formed, whether monomeric or oligomeric. Thus it has been reported [10,15] that the heaviest lanthanides form phthalocyanine complexes with fewer phthalocyanine units per lanthanide ion while the lighter lanthanides form complexes with higher number of phthalocyanine units with lanthanum and neodymium being predominant in this regard.

There has been a lot of attention on the oligomeric lanthanide phthalocyanines, with only a few reports on the monomeric derivatives [16]. The current work is thus devoted to synthesis, photochemical and photophysical study of novel phenoxy-substituted phthalocyanine complexes of the heavier lanthanides (Dy, Er and Lu), by direct chemical reaction with initial phthalonitrile–metal ratio of 4:1 and reaction of the metal free phthalocyanine with the excess of the metal salt, with the view of forming monomeric phthalocyanines as major reaction products. The complexes are: 1(4), 8(11), 15(18), 22(25)-(tetraphenoxypthalocyaninato) lutetium(III) acetate (**4**) and 1(4), 8(11), 15(18), 22(25)-(tetraphenoxypthalocyaninato) erbium(III) chloride (**6**). Attempts to synthesize the monomeric dysprosium phthalocyanine resulted in bis-{1(4), 8(11), 15(18), 22(25)-(tetraphenoxypthalocyaninato)} dysprosium(III) complex (**5**), Scheme 1. The synthesis of a lanthanide phthalocyanine containing phenoxy groups at the non-peripheral position is reported for the first time as well as the photophysical behavior of the complexes.

2. Experimental

2.1. Materials

The following chemicals were purchased from SAARCHEM; 1-pentanol, *n*-hexane, tetrahydrofuran (THF), dimethyl sulfoxide

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