

Synthesis and solvent effects on the electronic absorption and fluorescence spectral properties of substituted zinc phthalocyanines

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Abstract

The synthesis and spectroscopic properties of the following tetra- and octa-substituted aryloxy zinc(II) phthalocyanines are reported for the first time: 1,(4)-(tetrabenzoyloxyphenoxyphthalocyaninato) zinc(II) (**7**); 3,(3)-(tetrabenzoyloxyphenoxyphthalocyaninato) zinc(II) (**8**); 2,3-(octabenzoyloxyphenoxyphthalocyaninato) zinc(II) (**9**). The new compounds have been characterized by elemental analysis, IR, ¹H NMR spectroscopy and electronic spectroscopy. Spectroscopic properties of these compounds were investigated in different solvents. Protonation of non-peripherally substituted complex **7** resulted in the splitting and red-shifting of the Q-band. The peripherally substituted derivatives **8** and **9**, did not show the split in the Q-band. Fluorescence spectra of the derivatives show Stokes shifts typical of MPc complexes.

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1. Introduction

Phthalocyanines and metallophthalocyanines have been investigated in detail for many years because of their wide applications in many fields, including use and investigation in chemical sensors, liquid crystals, Langmuir–Blodgett films, nonlinear optics, optical data storage and as carrier generation materials in near-IR devices [1,2]. Substituted derivatives can also be used for photodynamic cancer therapy and other processes driven by visible light [1,2]. A decisive disadvantage of phthalocyanine and metal phthalocyanines is their low solubility in organic solvents or water. The solubility can be increased, however, by introducing alkyl or alkoxy groups into the peripheral and non-peripheral positions of the phthalocyanine framework [3].

Because of their lower degree of order in solid state, tetra-substituted phthalocyanines are more soluble than the corresponding octa-substituted ones. In contrast to octa-substituted systems, tetra-substituted phthalocyanines are obtained as a mixture of constitutional isomers by statistical synthesis starting from mono-substituted phthalonitriles or corresponding diiminoindolines. Depending on their substituent positions two types (non-peripherally and peripherally substituted) of tetra-substituted macrocycles which show significant differences in their chemical and physical behaviour can be obtained.

Recently, phthalocyanine complexes have found applications as photosensitisers in PDT since diamagnetic central metals, such as Zn or Mg enhance phototoxicity of phthalocyanines [4–7]. Zinc phthalocyanine complexes have attracted much interest because of their appreciably long triplet lifetimes [8–10]. Such long lifetimes constitute a great advantage since the number of diffusional encounters between the triplet excited state and ground state molecular oxygen increases with the lifetime of the excited

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