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Photoluminescence Properties of Tetra- and Octa-Substituted Double Decker Lu(III) Phthalocyanines

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Fluoreccence and photoluminescence properties of tetra and octa-substituted double decker Lu(III) phthalocyanines to which imidazole groups are attached have been investigated under the same conditions. The changes in these properties were examined with increasing number of substituents. Thus, the effect of imidazole groups on the optical properties of double decker Lu(III) phthalocyanines were determined. The photoluminescence spectra of the compounds show indicating the strong π-π interaction along with electron and energy transition between the tetrapyrolic macrocycles.

Keywords: Double-decker phthalocyanine, Photoluminescence, Fluorescence, Optoelectronics

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1. Introduction

Phthalocyanine with stable π-conjugated system is a synthetic analogue of porphyrin macrocycle. Phthalocyanines are organic semiconductor compounds. The intense blue-green color of phthalocyanines, combined with their thermal and chemical stability, has gained importance in many areas of application. Phthalocyanines with stable π-conjugated systems are of interest in many applications because of their photo-sensitivity, high fluorescence quantum yield, and strong absorption at high wavelengths such as 600-750 nm [1-6]. Phthalocyanines draw interest as materials for optical recording media, nonlinear optical application, light absorption, electric conduction, photoconduction, energy conversion, electrodes, chemical sensors and catalyst [3,7-9]. Phthalocyanines are known for their very poor solubility in many solvents. This property seriously limits potential applications of these compounds. Their solubility can be increase by substituents and metals. The substituted groups may be attached to the phthalocyanine ring at peripheral, non-peripheral or axial positions [1].

Double-decker ftalosiyanin metal complexes, in which two rings of phthalocyanine are coupled by a metal ion, shows high chemical and thermal stability, redox activity and intriguing optical, electrical and magnetic properties [3,10-12]. These properties allow double-decker phthalocyanines to become promising organic molecule candidates for optical materials and devices such as optical logic displays, electrochromic display, photovoltaic cells, and organic light emitting diodes [7,13,14]. Double-decker phthalocyanine complexes, known as stable radicals, with an uncommon electron in the delocalized π- orbital on two phthalocyanine rings, can be formulated as $Ln^{3+}(Pc^{2-})(Pc^{-})$ or $Ln^{3+}(Pc_2)^{3-}$. Strong π-π interactions are observed in such structures [3]. Lanthanide ions are also well known for their particular photoluminescent characters [10,11]. Photoluminescence spectra can be used to obtain information about the optical properties of these compounds [15,16].

It is desirable that organic semiconductor compounds to be used in optoelectronic applications do not exhibit aggregation behavior, have high fluorescence quantum yield, have absorbtion at high wavelengths and have appropriate orbital levels to permit electron transfer [5,17,18].

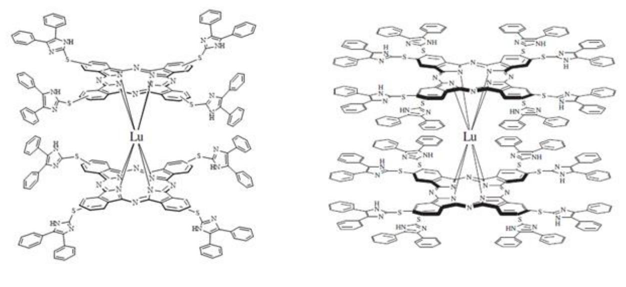
In this work, we examined the photoluminescence (PL) and fluorescence properties of tetra- and octa-substituted double decker Lu(III) phthalocyanine compounds. We have determined that these compounds have the potential to be used in optoelectronic applications.

2. Experimental details

The tetra- [19] and octa-substituted [20] double decker phthalocyanine compounds were prepared according to the literatures (Figure 1). Spectroscopic purity solvents were used in the whole study. Andor-Solis UNIRAM Raman and Fotoluminescence spectrometer was used for PL measurements of thin films. UV-vis spectra were recorded on a Shimadzu UV-1800 UV-vis spectrophotometer. A Shimadzu RF 5301 fluorescence spectrophotometer was used for spectrofluorometric measurements of solutions. Scanning Electron Microscope (SEM) images were taken at Tescan MIRA3 XMU. Thin films of the compounds were prepared by drop casting method. In this method, the compounds were dissolved separately in THF, the solutions were dropped onto the glass surface and allowed to dry.

3. Results and discussion:

The phthalocyanine compounds used in this study are tetra- and octa-substituted double decker phthalocyanine compounds whose molecular structures are shown in Figure 1. Photoluminescence and fluorescence properties of these compounds were investigated and their potential to be used in optoelectronic applications was determined. In addition, the aggregation properties of thin films of the compounds were examined by UV-vis spectrophotometer and the surface properties of the solids of the compounds were examined by SEM.



Tetra-substituted double-decker Lu(III) phthalocyanine

Octa-substituted double-decker Lu(III) phthalocyanine

Figure 1. *Molecular structures of tetra- and octa-substituted double decker phthalocyanine compounds*

PL properties of the compounds were examined by thin films prepared by drop casting method. The PL spectra of the compounds are shown in figures 2 and 3. The energy gaps for tetra- and octa-substituted lutetium(III) phthalocyanines were 1.73 eV and 1.72 eV, respectively. No significant difference was observed between the energy gaps of the compounds.

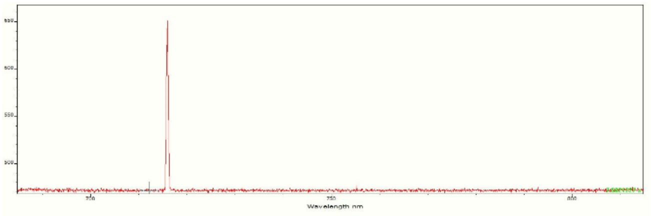


Figure 2. PL spectra of thin film tetra-substituted lutetium(III) phthalocyanine.

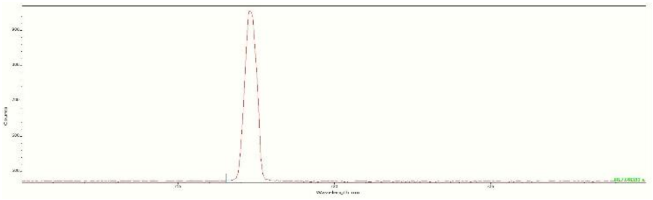


Figure 3. PL spectra of thin film octa-substituted lutetium(III) phthalocyanine.

The fluorescence properties of compounds in solution phase were examined (Figures 4 and 5).

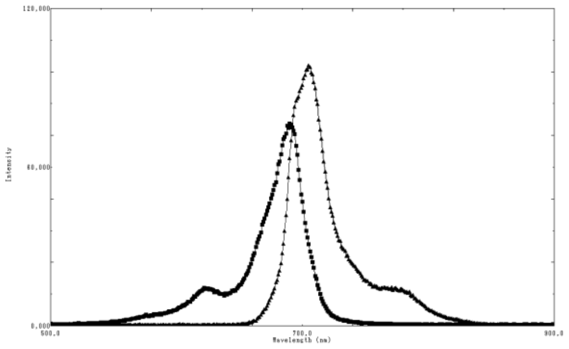


Figure 4. *Emission and excitation spectra of tetra-substituted lutetium(III) phthalocyanine.*

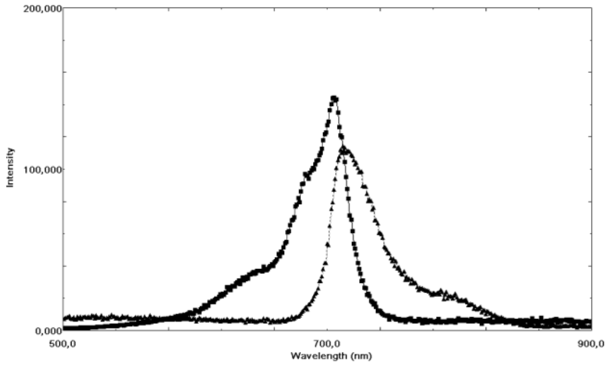


Figure 5. *Emission and excitation spectra of octa-substituted lutetium(III) phthalocyanine.*

Fluorescent quantum yields were calculated from measured emission spectra of compounds. The fluorescence quantum yields of compounds were determined by a comparative method in equation 1.

$$\Phi_\mathrm{F} = \Phi_\mathrm{F}(\mathrm{Std})\frac{FA_\mathrm{Std}\eta^2}{F_\mathrm{Std}A\eta^2_\mathrm{Std}} \qquad (1)$$

Where F and F_{Std} are the areas under the fluorescence emission curves of the compound and the standard, respectively. A and A_{Std} are the absorbance of the samples and standard at the excitation wavelength, respectively, η and η_{Std} are the refractive indexes of solvents used for compound and standard, respectively. Unsubstituted ZnPc was used as standard (Φ_F = 0.18 in DMSO) [21].

Fluorescence quantum yields for tetra- and octa-substituted double decker Lu(III) phthalocyanines were found to be 0.30 and 0.39, respectively. Binding of imidazole groups to phthalocyanine macrocycle significantly changed the fluorescence quantum yield and this difference increased as the imidazole groups increased. Imidazole groups appear to contribute to phthalocyanine in energy transfer.

Aggregation behaviors of these compounds in solution phase were investigated with UV-vis spectrophotometer. In addition, the aggregation behavior of these compounds in solid phase thin films were also examined (Figure 6). No significant shift or new peak formation was observed in the UV-vis spectra. Therefore, we can say that the compounds did not show aggregation behavior.

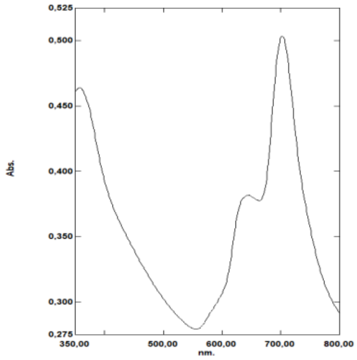


Figure 6. *UV-Vis spectrum of thin film tetra-substituted lutetium(III) phthalocyanine.*

The SEM images were also taken in solid form of tetra- and octa-substituted double decker Lu(III) phthalocyanine compounds. As observed from the SEM images, a more regular solid surface was obtained as a result of the increase of substituted imidazole groups (Figure 7).

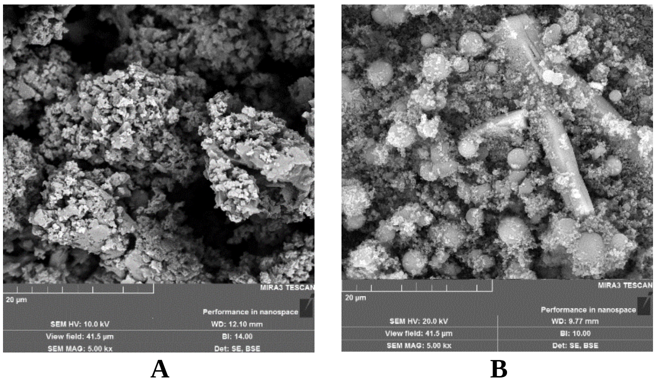


Figure 7. *SEM images of (A) tetra-substituted and (B) octa-substituted double decker Lu(III) phthalocyanines solids.*

Conclusions

In this study, we examined the photoluminescence and fluorescence properties of tetra- and octa-substituted double decker Lu(III) phthalocyanine compounds. The changes in these properties were examined with increasing number of substituents. The photoluminescence spectra of the compounds show indicating the strong π-π interaction along with electron and energy transition between the tetrapyrolic macrocycles. It was observed that the fluorescence quantum yield of the compounds was much higher than that of the standard unsubstituted phthalocyanine compound and increased as the number of substituted imidazole groups increased. Compounds also showed no significant aggregation. As the substituted imidazole groups increases, the molecule becomes more organized and has been superior properties. According to the results, these compounds have the potential to be used in optoelectronic applications.

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