



Synthesis, characterization, mesomorphic and electrical properties of tetrakis(alkylthio)-substituted lutetium(III) bisphthalocyanines

Devrim Atilla^a, Necmettin Kiliç^b, Fatma Yuksel^a, Ayşe Gül Gürek^a,
Zafer Ziya Öztürk^{b,c}, Vefa Ahsen^{a,c,*}

^a Gebze Institute of Technology, Science Faculty, Department of Chemistry, P.O. Box 141, 41400 Gebze-Kocaeli, Turkey

^b Gebze Institute of Technology, Science Faculty, Department of Physics, P.O. Box 141, 41400 Gebze-Kocaeli, Turkey

^c TÜBİTAK-Marmara Research Center, Materials Institute, P.O. Box 21, 41470 Gebze-Kocaeli, Turkey

ARTICLE INFO

Article history:

Received 17 July 2007

Received in revised form 19 June 2008

Accepted 14 July 2008

Available online 4 September 2008

Keywords:

Lutetium phthalocyanine

Lanthanide

Thin films

Dark current conductivity

Liquid crystal

ABSTRACT

The synthesis of new lutetium(III) bisphthalocyanines substituted with alkylthio groups (**1–5**) is described. These compounds (Pc₂Lu) are soluble in most common organic solvents and have been fully characterized (elemental analysis, FT-IR, UV–Vis spectroscopy, mass spectrometry). The thermal stabilities of the Pc compounds were determined by thermogravimetric analysis (TGA). The mesogenic properties of these new materials forming columnar-hexagonal (Col_h) mesophases were studied by differential scanning calorimetry (DSC), optical microscopy and X-ray diffraction. The compounds **2–5** exhibit a double clearing point. DC electrical properties of these compounds in different phases were determined by measuring *I–V* characteristics and dark current of their thin films on interdigital electrodes. The measurements were carried out in ambient air, in vacuum and in high purity nitrogen (N₂) flow in the temperature range between 300 and 420 K. Dark current measurements obtained in the crystal, liquid crystal (LC) and isotropic liquid phases were in agreement with the phase transitions of these compounds obtained by DSC and optical microscopy results. The relation between the phase transition and conductivity of the Pc₂Lu derivatives were investigated. Also, the influence of the nature of the substituted group (alkylthia and alkoxy) upon the DC electrical properties of the Pc₂Lu derivatives was investigated. The DC conductivities and the thermal activation energies depending on alkyl chain lengths of these compounds were found to be in the range of 10^{–8} to 10^{–5} S/cm and 0.12–0.38 eV in solid phase.

Crown Copyright © 2008 Published by Elsevier B.V. All rights reserved.

1. Introduction

Phthalocyanines (Pcs) have been widely used as dyes and pigments due to their high thermal and chemical stability. They now draw interest as materials for optical recording media, nonlinear optical application, light absorption, electric conduction, photoconduction, energy conversion, electrode, chemical sensor and catalyst, which make them unique substrates for new materials [1–3].

Pc is well known as a disc-like molecule and its forms a one-dimensional columnar structure in condensed phases. Pc mesogeneity was first demonstrated on alkoxymethyl-substituted copper phthalocyanine in 1982 [4]. The liquid-crystalline properties of Pcs depend on the number, position, and character of substituents and the nature of the central metal atom. The aromatic

ring can be considered as the core of a discotic mesogen, forming a supramolecular structure and resulting columnar mesophases. It has been found that numerous Pc derivatives which are peripherally or non-peripherally *octa*- and *tetra*-substituted with alkyl- [5], alkoxy- [6], alkoxymethyl- [4], oligo(ethyleneoxy) [7], alkylthia [8], oligo(ethyleneoxy)thia [9], and alkylthiamethyl [10] groups exhibit thermotropic or lyotropic mesomorphism. Liquid-crystalline Pcs offer the possibility of combining the optoelectronic properties of Pcs with the orientational control of conventional liquid-crystal systems. The columnar architecture of the mesophase suggests the possibility of using them as anisotropic conductors [11].

Among the large family of phthalocyanines, double-decker phthalocyanines and especially the lutetium derivatives have been subject to extensive investigations because of their possible use in gas sensing applications as well as photovoltaic and organic electronic devices. Bis(phthalocyaninato)lutetium (Pc₂Lu) and lithium phthalocyanine are the first known examples of intrinsic molecular semiconductors [12]. They show exceptionally high intrinsic conductivity when compared to most other compounds [13]. Pc rare-earth metal sandwich complexes substituted with long

* Corresponding author at: Gebze Institute of Technology, Science Faculty, Department of Chemistry, Gebze-Kocaeli 41400, Turkey. Tel.: +90 262 6053106; fax: +90 262 6538490.

E-mail address: ahsen@gyte.edu.tr (V. Ahsen).

peripheral chains are well-known for their columnar mesophases [14]. These columnar mesomorphic Pc derivatives are very attractive because of their one-dimensional charge transport properties [15]. Alkylthio-substituted Pcs display higher conductivities than their alkoxy-substituted Pcs in their mesophases [16,17].

The electrical properties of substituted lutetium bisphthalocyanines are not so thoroughly investigated. The series of bis[octakis(alkylthio)phthalocyaninato] rare-earth metal double-decker complexes were synthesized and their mesomorphism and charge transport by means of pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) were investigated [16]. Simon and co-workers have studied *octa*-alkoxy-substituted bis(phthalocyaninato)lutetium derivatives in the condensed phase (solid, liquid crystalline, and isotropic phases) over the frequency range 1 MHz to 100 kHz as a function of temperature [18]. The relationship between the structure of the lutetium bisphthalocyanine thin films evaporated under vacuum and their electrical conductivity were studied by Simon and co-workers [19]. The electrical properties of spin-coated bis(double-decker lutetium(III)phthalocyanine) and novel *tert*-butylcalixarene bridged bis(double-decker lutetium(III) phthalocyanine) thin films as a function of temperature were also investigated [20]. The effect of differences in structural organization on the electrical properties of spin-coated lutetium bisphthalocyanine $[\text{Lu}(\text{PcR}_8)_2]$ ($\text{R}=\text{SC}_6\text{H}_{13}$) were investigated by Basova et al. [21]. Up to date the syntheses of a variety of octa substituted double-decker lutetium Pcs were reported. Nevertheless, there have been only a limited number of reports on syntheses of tetra-substituted lutetium bisphthalocyanines [20,22,23].

In this work, we synthesized a series of bis[tetrakis(alkylthio)phthalocyaninato]lutetium(III) complexes, $[(\text{C}_n\text{H}_{2n+1}\text{S})_4\text{Pc}]_2\text{Lu(III)}$ ($n=6, 8, 10, 12, 16$) and investigated their mesomorphism and DC electrical properties in the first isotropic, liquid crystalline and solid phases.

2. Experimental

2.1. Synthesis

2.1.1. Materials and methods

1-Hexylthio-4,5-dicyanobenzene [24], 1-octylthio-4,5-dicyanobenzene [25], 1-decylthio-4,5-dicyanobenzene [26], 1-dodecylthio-4,5-dicyanobenzene [16], and 1-hexadecylthio-4,5-dicyanobenzene [27] were synthesized according to published procedures. Bis[tetrakis(dodecylthio)phthalocyaninato]lutetium(III) (**4**) [23] was also synthesized using the reported procedures. All other reagents and solvents were obtained from commercial suppliers and dried as described in Perrin and Armarego [28] before use.

2.1.2. Characterization

Elemental analyses were obtained using a Thermo Finnigan Flash 1112. Infrared spectra in KBr pellets were recorded on a Bio-Rad FTS 175C FT-IR spectrometer. Mass spectra were recorded on a VG Zab Spec GC-MS spectrometer using a liquid secondary ion mass spectrometer (LSIMS) and LCQ-ion trap (Thermo Finnigan) using electrospray ionisation (ESI) technique. ^1H and ^{13}C NMR spectra were recorded on a Varian 500 MHz spectrometer. Thermogravimetric analyses were carried out on Mettler Toledo Star^c Thermal Analysis System DSC 822e at a rate of $10^\circ\text{C min}^{-1}$ in a nitrogen flow (50 mL min^{-1}). Transition temperatures were determined with a Leitz Wetzler Orthoplan-pol equipped with a hot stage (Linkam TMS 93) and temperature-controller (Linkam LNP). Transition temperatures were determined with a scan rate of 5°C min^{-1} using the

same Mettler Toledo Star^c Thermal Analysis System. The differential scanning calorimeter system was calibrated with indium from 3 to 4 mg samples under nitrogen atmosphere. High-temperature X-ray diffraction measurements (Cu K α -radiation) were performed using a Rigaku Kristalloflex diffractometer (D/max 2200) equipped with a thermoregulator. The UV/Vis optical spectra in solution were recorded with a Shimadzu 2001 UV Pc spectrophotometer using 1 cm path length cuvettes at room temperature. The reduced forms of the Pcs **1–5** were prepared by adding 2 mg of NaBH_4 to 10 mL of a solution of the Pc ($4.71 \times 10^{-6}\text{ M}$) in THF under argon atmosphere. The oxidized forms of compounds **1–5** were obtained by adding bromine in CHCl_3 (20 μL , 0.097 M) to 10 mL of a chloroform solution of the Pc ($4.71 \times 10^{-6}\text{ M}$).

2.1.3. Synthesis

A strict experimental work-up has been used to add the different side chains. General procedure for experimental details will be given for the compound **1**.

2.1.3.1. Bis[tetrakis(hexylthio)phthalocyaninato]lutetium(III) (**1**).

A round-bottomed flask fitted with a condenser was degassed and flame-dried under dry argon. The flask was charged under argon with the nitrile derivative (1.82 g, 7.43 mmol), anhydrous $\text{Lu}(\text{OAc})_3$ (0.40 g, 1.14 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (600 μL , 4 mmol), and 16 mL of pentan-1-ol. The mixture was refluxed under argon for 48 h. Evaporation of the pentan-1-ol under reduced pressure left a green waxy product. It was dissolved and heated under reflux in methanol (30 mL) and then separated by decantation. This purification step was repeated three times. Further purification was achieved by column chromatography (silica gel; eluent $\text{CH}_2\text{Cl}_2/n$ -hexane, 1:1 (v/v)). Yield: 250 mg (% 12). $\text{C}_{112}\text{H}_{130}\text{LuN}_{16}\text{S}_8$ (2130); Found C, 63.20; H, 6.17; N, 10.60%; required C, 63.10; H, 6.15; N, 10.51%; IR (KBr): ν_{max} (cm^{-1}) 3020, 2954–2854(CH_2 , CH_3), 1598($\text{C}=\text{N}$), 1510, 1455, 1310, 1261, 1068, 952, 907. MS (LSIMS), m/z (%): 2130 (100) $[\text{M}]^+$, 2045(25) $[\text{M}-(\text{C}_6\text{H}_{13})]^+$.

2.1.3.2. Bis[tetrakis(octylthio)phthalocyaninato]lutetium(III) (**2**).

Yield: 317 mg (% 14). $\text{C}_{128}\text{H}_{162}\text{LuN}_{16}\text{S}_8$ (2355); Found C, 62.10; H, 6.77; N, 9.60; requires C, 62.25; H, 6.93; N, 9.51; IR (KBr): ν_{max} (cm^{-1}) 2924–2853(CH_2 , CH_3), 1600($\text{C}=\text{N}$), 1512, 1454, 1314, 1260, 1073, 950, 908. MS (ESI-MS), m/z (%): 2357(100) $[\text{M}+2]^+$.

2.1.3.3. Bis[tetrakis(decylthio)phthalocyaninato]lutetium(III) (**3**).

Yield: 310 mg (% 13). $\text{C}_{144}\text{H}_{194}\text{LuN}_{16}\text{S}_8$ (2579); Found C, 67.10; H, 7.77; N, 8.60; required C, 67.00; H, 7.58; N, 8.64; IR (KBr): ν_{max} (cm^{-1}) 2923–2852(CH_2 , CH_3), 1598($\text{C}=\text{N}$), 1511, 1454, 1310, 1260, 1068, 951, 908. MS (ESI-MS), m/z (%): 2582(100) $[\text{M}+3]^+$.

2.1.3.4. Bis[tetrakis(dodecylthio)phthalocyaninato]lutetium(III) (**4**).

Yield: 215 mg (% 8.1). $\text{C}_{160}\text{H}_{224}\text{LuN}_{16}\text{S}_8$ (2802); Found C, 69.00; H, 7.98; N, 7.95; required C, 68.56; H, 8.05; N, 8.00; IR (KBr): ν_{max} (cm^{-1}) 2960–2860(CH_2 , CH_3), 1600($\text{C}=\text{N}$), 1511, 1456, 1305, 1260, 1070, 910, 920. MS (LSIMS), m/z (%): 2802(100) $[\text{M}]^+$, 2634 (35) $[\text{M}-\text{C}_{12}\text{H}_{25}]^+$, 2469 (8) $[\text{M}-2(\text{C}_{12}\text{H}_{25})]^+$.

2.1.3.5. Bis[tetrakis(hexadecylthio)phthalocyaninato]lutetium(III) (**5**).

Yield: 360 mg (% 12). $\text{C}_{192}\text{H}_{290}\text{LuN}_{16}\text{S}_8$ (3252); Found C, 70.70; H, 8.97; N, 7.00; requires C, 70.87; H, 8.98; N, 6.89; IR (KBr): ν_{max} (cm^{-1}) 2922–2851(CH_2 , CH_3), 1599($\text{C}=\text{N}$), 1511, 1456, 1311, 1260, 1068, 951, 907. MS (ESI-MS), m/z (%): 3255(100) $[\text{M}+3]^+$.

Download English Version:

<https://daneshyari.com/en/article/1443215>

Download Persian Version:

<https://daneshyari.com/article/1443215>

[Daneshyari.com](https://daneshyari.com)