Polyhedron 30 (2011) 1023–1026

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Temperature activated ionic conductivity in gallium and indium phthalocyanines

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ARTICLE INFO

Article history:
Received 18 November 2010
Accepted 31 December 2010
Available online 11 January 2011

Keywords:
Dielectric spectroscopy
Activation energy
Phthalocyanines
Semiconductors

ABSTRACT

The effects of introducing gallium and indium metals into phthalocyanine molecules were investigated via temperature and frequency dependent dielectric spectroscopy. The dielectric properties of Ga(III) and In(III) phthalocyanine pellets were measured at frequencies from 1 kHz to 1 MHz in the temperature range 300–530 K. The temperature dependence of the real part of the dielectric constant suggested that these compounds exhibit semiconductor behavior. The activation energy values were calculated from the Arrhenius plots at different frequencies. A distinct transition in these plots indicated the activation of ionic conductivity at higher temperatures.

1. Introduction

Metallophthalocyanines (MPcs), a family of aromatic macrocycles based on an extensive delocalized 18-π electron system, are known not only as classical dyes in practical use but also as modern functional materials in scientific research. There is a growing interest in the use of phthalocyanines (Pcs) in a variety of applications, including non-linear optics [1], semiconductor devices [2], Langmuir–Blodgett films [3], electrochromic display devices [4], liquid crystals [5] and as photosensitizers in photodynamic therapy (PDT) [6]. For non-linear optical applications, MPcs have advantages over the currently used inorganic compounds due to their small dielectric constants [7], fast response times, ease of processability into optical components and their lower cost [1,7]. The structures of MPcs can be modulated in many ways, by changing the peripheral and non-peripheral substituents on the ring in addition to changing the central metal and the axial ligands.

Heavy metals, especially diamagnetic metals, play a major role in photosensitizing and optical limiting mechanisms because they enhance intersystem crossing through spin orbit coupling. This enhancement is desirable as it improves the probability of forming a large population in the triplet state. Axial ligands in MPcs play a key role in preventing or minimizing intermolecular interactions, which causes aggregation in solution. Aggregation can result in the fast decay of excited states. Indium and gallium are useful central metals in MPcs complexes since they are diamagnetic and are able to host axial ligands. Gallium and indium phthalocyanines have been reported to have good photosensitizing and optical limiting properties [1,7–11].

In the scope of this work, chlorogallium (ClGaPc) and chloroindium (ClInPc) phthalocyanine samples were examined with dielectric spectroscopy (DS). This method is shown to be a reliable tool for investigating molecular scale events and for the optimization of tailored materials [12–14]. The temperature dependence of the real part of their dielectric constants and dielectric loss were measured and analyzed. Activation energies of ClGaPc and ClInPc samples were also calculated at different frequencies. The conductivities and the activation energies of the samples increased at elevated temperatures, which were attributed to the activation of the ionic conductivity with increasing temperature.

2. Experimental

2.1. Sample preparation

2.1.1. ClGaPc

This compound was synthesized and characterized according to the method reported elsewhere [15]. Briefly, a mixture of phthalonitrile (5 g, 0.04 mol), anhydrous gallium trichloride (5.5 g, 0.03 mol), and 20 mL of quinoline (double distilled over CaH_2, deoxygenated) was refluxed for 1 h (particular attention was paid to the exclusion of water during this step). After cooling the mixture to approximately 273 K, the reaction mixture was filtered. The mixture was washed with toluene and methanol and dried at 383 K. The final solid compound had a purple color. Yield: 3.4 g (55%). *Anal.* Calc. for $C_{32}H_{16}N_8GaC1$: C, 62.22; H, 2.61; N, 18.14. Found: C, 62.75; H, 2.34; N, 18.89%.

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doi:10.1016/j.poly.2010.12.047