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Synthesis and refractive index dispersion properties of the N,N',N''-trinaphthylmethyl melamine–DDQ complex thin film

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Abstract

The synthesis and optical properties of the N,N',N''-trinaphthylmethyl melamine–DDQ complex thin film were investigated by the optical characterization. The optical constants such as refractive index and absorption coefficient were determined and the refractive index dispersion was analyzed by the single-effective oscillator model. The single oscillator energy E_o and the dispersion energy E_d were calculated. The effect of temperature on refractive index dispersion and optical band gap is also discussed. Consequently, the annealing temperatures have an important effect on the absorption edge and refractive index of the thin film.

Keywords: Optical constant; Single oscillator; Annealing temperature

1. Introduction

Melamine (2,4,6-triamino-1,3,5-triazine) has a wide application in industry. The solid state complexation of melamine with different acids has an interesting aspect concerning the hydrogen bond system formed [1]. High nitrogen containing compounds are interest because of thermally stable materials for high temperature applications, oxidative stability and advanced materials [2]. Substituted *s*-triazines have a wide application range in optoelectronics, telecommunications and biological activities such as antibacterial [3,4].

Charge transfer (CT) interactions within a molecular complex forming an electron donor and electron acceptor involving a resonance with a transfer of charge from donor to acceptor were showed by Mulliken [5]. Formation of charge transfer complexes (CTC) is based on the interaction of energetically high lying HOMO of the donor with a low energy LUMO of the acceptor. In general, the charge transfer complexation occurs as an ionic band in a simple ion–radical pair interaction.

Molecular charge transfer materials became an attractive and realistic target for materials science to research for molecular CT systems accompanied with the changes in magnetic, transport optical, dielectrical properties and structural changes. CT complexes which exhibit interesting optical, electrical and photoelectrical properties play an important role in many electro physical and optical processes [6].

Aliphatic amines, aromatic amines, aromatic hydrocarbons and aromatic hetero cycles are the major organic donors. In the present work, N,N',N''-trinaphthyl melamine was used as donor molecule and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) was used as acceptor molecule. During the CT complexation, N,N',N''-trinaphthylmethyl melamine has both n–π^* and π–π^* electronic transitions.

This paper reports optical and refractive index dispersion properties of the N,N',N''-trinaphthylmethyl melamine–DDQ complex thin film.

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2. Experimental

2.1. The preparation of 1-chloromethyl naphthalene

1-chloromethyl naphthalene was prepared according to the literature [7]. In a 500 ml three-necked flask, fitted with a reflux condenser and magnetic stirrer, are placed 25.6 g (0.2 mol) of naphthalene, 11.0 g of para formaldehyde, 26.0 ml of glacial acetic acid, 16.5 ml of 85% phosphoric acid, and 42.8 g (36.2 ml, 0.42 mol) of concentrated hydrochloric acid. This mixture is heated in a water bath at 80–85 °C and vigorously stirred for 6 h.

After the mixture has been cooled to 15–20 °C, it is transferred to a 500 ml separatory funnel and the crude product is firstly washed with two 200 ml portions of water cooled to 5–15 °C, then with 100 ml of cold 10% potassium carbonate solution, and finally with 100 ml of cold water. The product is the lower layer in all the washings. After the addition of 30 ml of ether, the solution is given a preliminary drying by being allowed to stand over 1.0 g of anhydrous potassium carbonate, with frequent shaking, for 1 h. The lower aqueous layer formed is separated, and the ether solution is again dried over 3.0 g of potassium carbonate for 10 h.

The dried solution is distilled, first at atmospheric pressure to remove most of the solvent, and then under reduced pressure. A fore-run of unused naphthlene amounting to 4.0 g is collected at 90–110 °C/5 mm. This is followed by 20 g of 1-chloromethyl naphthalene which boils at 148–153 °C/14 mm. (75% based on naphthalene consumed).

2.2. The preparation of N,N′,N″-trinaphthylmethyl melamine

In a 100 ml two-necked flask, fitted with a reflux condenser and magnetic stirring bar is charged with 20 ml of dimethyl sulfoxide and 0.739 g (0.0132 mol) of potassium hydroxide. The mixture is stirred at room temperature for 15 min. 0.277 g (0.0022 mol) of melamine in dimethyl sulfoxide is added to this mixture. Stirring is continued for 15 min before 1.17 g (0.0066 mol) of 1-chloromethyl naphthalene in dimethyl sulfoxide is added dropping slowly. The mixture is refluxed at 80 °C for 14 h. After cooling down to room temperature, the mixture was diluted with 600 ml of water and filtered and dried. *N*,*N*′,*N*″-trinaphthylmethyl melamine was purified by column chromatography using silica gel and dichloromethane–hexane eluting fractionally yielded 0.35 g (30%) creamy powder.

2.3. The preparation of N,N′,N″-trinaphthylmethyl melamine–DDQ complex thin film

Chemical structures of materials used in this work are shown in Fig. 1. Charge transfer complexes determined as 3:1 stochiometric ratio (donor:acceptor ratio) by the job method [8] has been prepared with the interaction of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone(DDQ) and *N*,*N*′,*N*″-trinaphthylmethyl melamine in dichloromethane at room temperature.

The film of the compound was prepared by evaporating the solvent from a solution of the compound with subsequent drying of the film deposited on quartz substrate. The solution of the compound was homogenized for 5 h and was rotated for homogeneous mixing. The film thickness was obtained as ∼110 nm [9,10]. The film was annealed at different temperatures (50, 80, 110 and 140 °C) for 30 min [11,12].

The UV–Visible spectra of the thin film were recorded by Shimadzu UV-2401 PC UV–Visible recording spectrophotometer at room temperature. Analysis of the absorption coefficient was also carried out to determine optical band gap and nature of transitions.

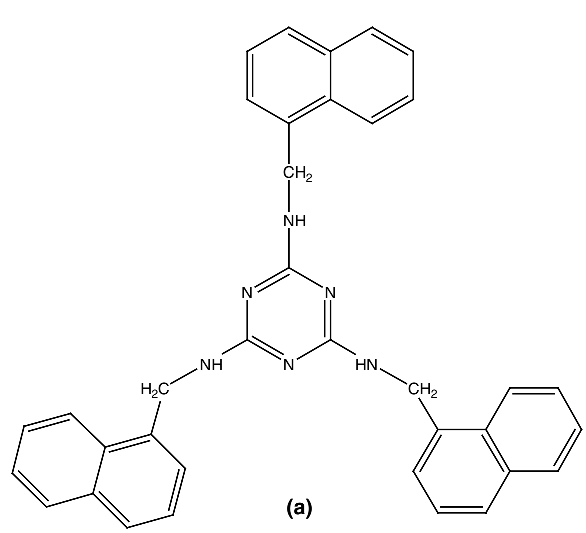

Fig. 1. Chemical structures of materials used in this work: (a) *N*,*N*′,*N*″-trinaphthylmethyl melamine; (b) DDQ(2,3-dichloro-5,6-dicyano-*p*-benzoquinone).