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Solvent free synthesis of a novel intermolecular compound and its crystal structure, thermal and optical studies

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ABSTRACT

Novel intermolecular compound (IMC) of anthranilic acid and dinitrobenzene has synthesized by solvent free synthesis and its large size single crystal has grown using solution growth technique and mixed solvent. The stoichiometry of the IMC was determined by phase diagram study. The spectral, single crystal XRD and atomic packing studies of the IMC confirmed the hydrogen bonding association between the parent compounds. The DSC of IMC showed a sharp melting peak at 141 °C, however TGA study confirms its thermal stability up to 220 °C. The solvent effects on the electronic absorption and fluorescence spectra of IMC have been studied as function of solvent polarity and their quantum yields are calculated in different solvents. The optical transmittance spectrum of as grown crystal of IMC shows 55% transparency however its energy band gap and refractive index are found to be 3.40 eV and 2.29, respectively.

1. Introduction

The organic crystalline materials are more demanding in modern science and technology for their versatile uses in fabrication of variety of nonlinear optical, electro-optic, semiconductor, laser and superconductor devices. The organic materials are quick in response time, possess high polarizability and offer wide scope in engineering of novel materials and have prompted researchers to explore the variety of novel organic materials of specific properties for their particular applications [1–5]. In recent years, the solvent free synthesis of advanced materials has emerged the concept of green synthesis and has been an integral part in material science [6]. The solid-state synthesis also covers wide range of advantages in terms of selectivity, stereochemistry, 100% yield, ease of recycling, ease of isolation of product and energy usage over the conventionally adopted solvent synthesis [7]. The tiny crystals could only serve the purpose of single crystal X-ray analysis and crystal structure determination while for study of various optical properties and device applications of materials, crystals of sufficient large size are required [8,9]. Furthermore, the molecular complexation has been found worth for synthesis of novel materials as well as for improving some of the drawbacks of organic materials [10,11].

Anthranilic acid (2-aminobenzoic acid) is used as a potential candidate for the synthesis of intermolecular compound due to its extensive intra and intermolecular hydrogen bonding, known for long fluorescence lifetime and high fluorescence quantum yield ($\Phi = 0.60$) in aqueous solution [12,13]. In the present paper, the solvent free synthesis of a novel intermolecular compound, IMC, has been done by taking anthranilic acid (AA) and 1, 3-dinitrobenzene (DNB) as parent compounds, and its large size single crystal has been grown. The grown crystal of IMC was studied for thermal, crystal structure, atomic packing and spectroscopic studies. The optical transparency, band gap and refractive index of novel IMC crystal are studies. The influences of polarity of solvents on the electronic absorption and fluorescence spectra of IMC have been performed and their quantum yields are calculated. Beside these studies, the different physicochemical studies; enthalpy of fusion, enthalpy of mixing, Jackson's roughness parameter and grain boundary energy of eutectics and IMC are also studied.

2. Experimental

2.1. Materials and purification

The parent compounds, anthranilic acid and 1, 3-dinitrobenzene, were purchased from Aldrich, Germany. The purity of each compound was accessed by comparing their melting points and NMR studies. The melting points of AA and DNB were found to be 147.0 and 91.0 °C, respectively which are in agreement with their literature value [14].

2.2. Phase diagram study

The phase diagram of AA-DNB system was determined by the thaw-melt method in the form of temperature–composition curve. In this

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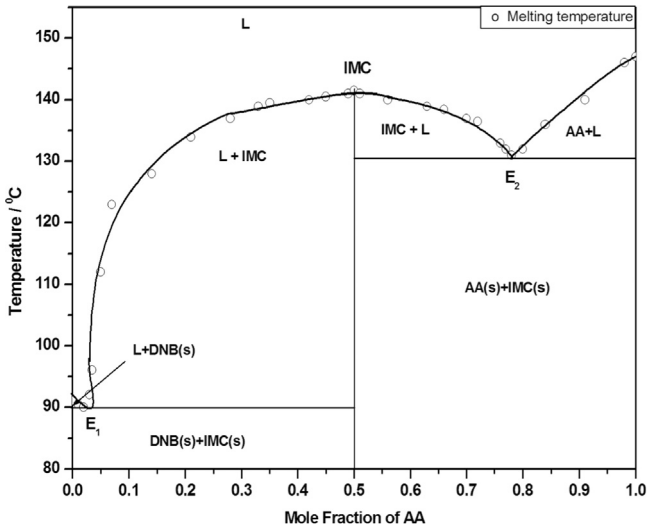

Fig. 1. Phase diagram of AA-DNB system.

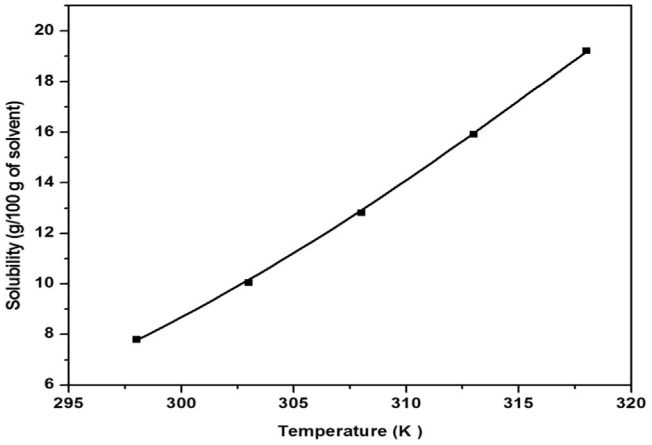

Fig. 2. Solubility curve for AADNB intermolecular compound.

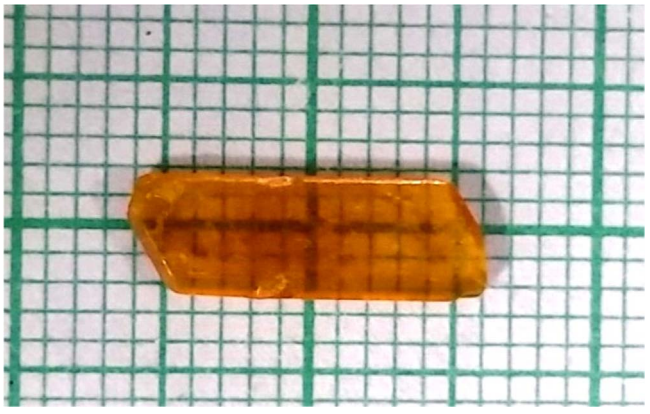

Fig. 3. Photograph of AADNB single crystal.

method [15] the binary mixtures of two parent compounds are taken in different molar ratio, covering the entire range of composition from 0.0 to 1.0 mol fraction of AA, in different test tubes and the mouth of these test tubes were sealed. The binary mixtures of each test tube were homogenized by melting in silicon oil bath maintained at a particular temperature 10 °C above than the melting temperature of the parent compounds having maximum melting temperature. These homogenized melts were suddenly chilled in ice cooled water and the process homogenization and chilling was repeated for 4 times for each test tube. The synthesized compounds thus were taken out separately and

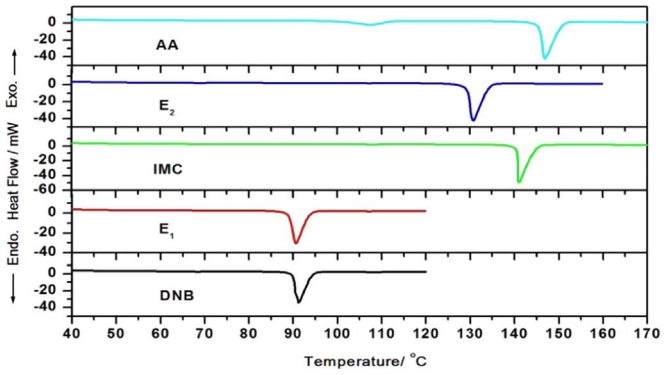

Fig. 4. DSC plot of AA, DNB, eutectics and intermolecular compound.

Table 1
Melting temperature, Heat of fusion, Heat of mixing and entropy of fusion of AA-DNB system.

Component	Melting temperature (K)	Heat of fusion (kJ mol^{-1})	Heat of mixing (kJ mol^{-1})	Entropy of fusion (kJ mol^{-1} K^{-1})
AA	420.0	23.20		0.055
DNB	364.0	16.72		0.046
Eutectic-1	363.0	Exp. 18.94 Cal. 17.88	1.06	0.052
Eutectic-2	404.0	Exp. 33.38 Cal. 33.18	0.20	0.082
Intermolecular compound (1:1 M ratio)	414.0	Exp. 45.88 Cal. 39.92	5.96	0.110

Table 2
Roughness parameter (α), interfacial energy (σ) and grain boundary energy (γ) of AA, DNB, eutectics and intermolecular compound.

Component	α	σ (erg cm^{-2})	γ (erg cm^{-2})
AA	6.65	45.41	90.82
DNB	5.52	30.86	61.72
Eutectic-1	6.27	31.15	62.30
Eutectic-2	9.93	42.21	84.42
IMC	13.32	38.11	76.22

Table 3
Excess thermodynamic functions for the eutectics of AA-DNB system.

Component	g^E (kJ mol^{-1})	h^E (kJ mol^{-1})	s^E (J mol^{-1} K^{-1})
Eutectic-1	0.2364	0.8840	0.0018
Eutectic-2	1.3212	21.3319	0.0495

crushed to fine powder. The melting points of each compositions were determined using Toshniwal melting point apparatus, attached with a thermometer which could read up to ± 0.5 °C and the phase diagram was established between the mole fraction composition of parent components on X-axis and their corresponding melting temperature on Y-axis.

2.3. Solubility measurement

The solubility of solvent free synthesized AADNB intermolecular compound was measured in mixed solvent of 1:1 volumetric ratio methanol-water at different particular temperatures from 298 K to 318 K. The solid IMC in 100 mL mixed solvent in a conical flask with stopper and a bar magnet was placed over a submersible stirrer and the