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Morphology and properties of thin films of diketopyrrolopyrrole derivatives

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1. Introduction

Organic electronic devices based on different types of organic semiconductors such as polymers, oligomers, dendrimers, dyes and pigments are already entering the commercial world. Among them the small organic molecule thin films are the subject of intense research activity as they provide high quality thin films and nanostructures. This paper deals with derivatives of 3,6-diphenyl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4 diones, commonly referred as DPP, which constitute a promising class of small molecular semiconductors. These compounds have been the object of intensive research for pigment application since 1974 as their exhibit a variety of shades in the solid state and especially chemical, light and thermal stability [1,2]. DPP itself has a high molar absorption coefficient, as well as high quantum vield of fluorescence, therefore low molecular weight derivatives of DPP have been extensively studied on their optical and photophysical properties [3–5]. Potential application of DPP derivatives as a luminescent media in a polymer matrices [6-8], solid-state dye lasers [9], OLED devices [10] and organic field-effect transistors [11] was reported. Recently a new application as hydrogen sensing material utilizing variable conductivity of DPP pyridyl derivative occurred [12].

Thin films of small molecular semiconductors are usually prepared by means of a variety of complex techniques including physical or chemical vapour deposition, organic molecular beam

ABSTRACT

Thin layers of five derivatives of 3,6-diphenyl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4 diones, which constitute a promising class of small molecular semiconductors, were investigated. The morphology of the thin layers prepared by both vacuum evaporation and spin casting were studied using Scanning Electron Microscopy and Atomic Force Microscopy. The relation between molecular structure and their thin films morphology was found. The electroluminescence behaviour of selected derivatives is also discussed with regard to morphology studies.

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epitaxy or solution-based deposition techniques. The performance of small molecular organic devices has been shown to be highly sensitive to film morphology and processing conditions. Often, the solution deposited active layers of devices (e.g. spin cast films) exhibit a high portion of microcrystallites and aggregates whereas the vapour deposition techniques provide high quality crystalline films, characterized by improved charge transport properties compared with those of solution deposited films. The relationship between the organic thin film morphology and the device performance is nowadays subject of the research activity.

In this study we investigated a group of five DPP derivatives depicted in Fig. 1. In order to increase solubility required for low cost solution-based casting, the basic DPP structure was modified by different alkyl substitutions on the nitrogen atoms. In addition, the electronic properties of one derivative (DPP VI) were altered by di-donor substitution.

Our previous studies based on quantum chemical calculations showed that both symmetrically (DPP III, DPP V, DPP VI) and nonsymmetrically (DPP II, DPP IV) substituted derivatives have rotated phenyl groups, as opposed to the non-substituted basic structure, which is nearly perfectly planar. The substitution of alkyl chain leads to the rotation of the adjacent phenyl group. The symmetrically substituted derivatives have thus rotated both phenyls. The rotation was independent on the length of the alkyl chain. These rotations subsequently modified absorption and photoluminescence spectra [13]. The theoretical results were confirmed by experimental optical characterization of solutions of selected derivatives. They showed that the increasing phenyl torsion leads to reduction of the conjugation extend and subsequently to a slight

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Fig. 1. Structure of basic DPP molecule and prepared derivatives and their temperatures of melting point.

hypsochromic shift of the absorption and bathochromic shift of the photoluminescence spectra as predicted from the calculations. The vibrational structure was less pronounced with increasing phenyl torsion and larger Stokes shift was observed. Simultaneously, the molar absorptivity decreased as the deformation increased. On the other hand, the measured fluorescence quantum yields were modified only slightly [13]. These properties, together with chemical, light and thermal stability predestine them as potential candidates for different optoelectronic applications. Therefore the film forming and electroluminescence properties of these materials were investigated and the question of relation between the chemical structure and morphology of prepared thin films was addressed.

2. Experimental

The DPP derivatives were synthesized and analyzed to confirm the molecule structure by A Bruker AMX 360 NMR spectrometer, ion trap mass spectrometer MSD TRAP XCT equipped with APCI, EA 1108 FISONS instrument for elemental analysis and Fourier transform infrared spectrometer (see [13] for details). Thin films were prepared by spin coating and by vacuum evaporation method. Low resistivity silicon substrates were used for morphology studies, whereas indium tin oxide (ITO) coated low alkali Corning glass was used for electro-optical and quartz glass for optical characterization. Thin layers spin-casted from chloroform-toluene solution (7:3) were typically 100-200 nm thick as measured by elipsometry. The vacuum deposition of 200 nm thick layers was carried out at a pressure of 1×10^{-4} Pa with deposition rate from 0.2 to 0.5 nm/s. The substrate temperature was maintained constant during the deposition process, being in the range 250-420 K. The annealing of the films was carried out in vacuum at various temperatures with regard to melting point of annealed substances. The morphology of the samples was investigated by Scanning Electron Microscopy (SEM) and by Atomic Force Microscopy (AFM). Multilayered sandwiched structures consisting of hole transport layer, emissive layer and electron transport layer were prepared for electroluminescence characterization. ITO covered glass substrates were used as transparent anodes. Subsequently, a hole-transporting layer of poly(3,4ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) and active electroluminescence layer of DPP derivative were spincasted. The structure was completed by vacuum deposition of electron-transporting layer of aluminium tris(8-hydroxyquinoline) (Alq₃) covered by vacuum deposited 100 nm thick aluminium top electrode.



Fig. 2. Comparison of the structure of the thin layers of the basic DPP material DPP I prepared at different substrate temperatures as probed by SEM: (a) 255 K, (b) 290 K, (c) 373 K and (d) 423 K.

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