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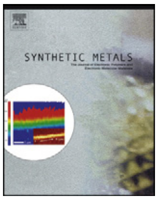

A study of thermal, optical and electrical properties of new branched triphenylamine-based polyazomethines

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ABSTRACT

A series of branched aromatic polyazomethines have been obtained by high temperature solution polycondensation of 4,4′,4″-triformyltriphenylamine with 3,3′-dimethoxybenzidine with different feed molar ratio. For three polymers additional condensation of chain end groups with monofunctional monomers such as 4-formyltriphenylamine or 2-naphthylamine was carried out. Moreover, two model compounds were prepared and investigated for comparison with branched polymers. The structures of polymers and models were characterized by means FTIR, ^{1}H, ^{13}C NMR spectroscopy, elemental analysis and gel permeation chromatography (GPC). UV–vis properties of the thin films of the polymers and compounds were investigated on the glass substrate. Eg of the branched polymers was found about 2.47 eV. UV–vis and FTIR spectroscopy for iodine doped compounds were investigated. Doping decreased the value of Eg of the branched polyazomethines to about 1.71 eV. Refractive index (n) for branched polyazomethines was found about 1.97, while for the doped compounds was a little higher (~2.48). Absorption (UV–vis) properties of the doped with iodine branched imines were investigated additionally after heating in different temperatures from 50 to 200 °C. Intensity of photoluminescence of branched imines in relation to 9,10-diphenylanthracene was found in the range 0.2–1.0% and 2.7–43.7% in dependence on the excitation wavelengths. Current–voltage (I–V) measurements were performed on ITO/TiO$_2$/polymer/Al, ITO/polymer/Alq$_3$/Al and ITO/TiO$_2$/polymer/Alq$_3$/Al devices in the dark and during irradiation with light (under illumination 1000 W/m^2). The sol–gel technique was applied to prepared TiO$_2$ layer. TiO$_2$ layers and devices were investigated by Atomic Force Microscopy (AFM). Moreover, properties of these branched polymers were compared with the linear polyazomethine based on 3,3′-dimethoxybenzidine and 4,4′-diformyltriphenylamine.

1. Introduction

Polyazomethines as a thermostable polymers are interesting candidates for opto(electronic) applications [1–9]. Among the huge class of polyazomethines, polymers with triphenylamine units are very attractive as hole transport materials for opto(electrical) applications [2–9]. For example, Niu et al. [2,3] studied polyazomethines obtained from 4,4′-diaminotriphenylamine and terephthalic aldehyde or glyoxal. Current–voltage measurements of a device having construction ITO/polymer/Alq$_3$/Al showed that green electroluminescence was clearly observed at a voltage about 5.4 V. The brightness increased superlinearly upon increase of the voltage, just like current. The maximum brightness reached up to 1.8 cd/m^2 at 36 V. Photoluminescence properties of a series of polyazomethines synthesized in polycondensation reaction of 4,4′-diformyltriphenylamine and various aromatic diamines were described by Sek et al. [4–7]. Nitro-substituted 4,4′-diformyltriphenylamine was used for condensation with aromatic diamines by Liou et al. [8] to obtain polyazomethines and to investigate their PL and electrochemical behaviors. Hindson et al. [9] investigated photovoltaic properties of triphenylamine-based polyazomethines obtained from 2,5-thiophenedicarboxaldehyde (Th), terephthalaldehyde (Ta) or 1,3-isophthalaldehyde (Iso) and 4,4′-diaminotriphenylamine (TPA). A photovoltaic device based on a TPA-Th/PCBM blend (1:3) under simulated sunlight gives an open-circuit voltage (V_{oc}) of 0.41 V, a short-circuit current (J_{sc}) of 1.23 mA cm^{-2} and a fill factor (FF) of 0.24, leading to a power conversion efficiency (η) of 0.12%. While for the TPA-Ta/PCBM blend

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(1:3) and TPA-Iso/PCBM blend (1:3) such photovoltaic parameters as V_{oc}, J_{sc}, FF and η have the following values, 0.42 V, 0.48 mA cm^{-2}, 0.22, 0.04% and 0.52 V, 0.19 mA cm^{-2}, 0.19, 0.02%, respectively.

Moreover, various structures of small molecules with triphenylamine unit have been presented by Shirota and Kageyama in the review paper [10]. Also branched polymers with triphenylamine units have attracted more interest due to their interesting properties. For example, Meng et al. [11] synthesized linear and tribranched copolymers with triphenylamine and vinyl-cyano groups for two-photon absorption and two-photon fluorescent materials. They found that the two-photon absorption cross-section of the branched polymer was nearly four times larger than that of the linear polymer. Wu et al. [12] investigated branched polymer with triphenylamine as a central core and polyfluorene branches and oxadiazole units in the side chains. The polymer emitted blue light and had LUMO and HOMO energy level at −2.50 eV and −5.27 eV, respectively. Hyperbranched copolymers containing triphenylamine and fluorene or thiophene moieties were investigated by Grigoras and Stafie [13]. The copolymer with fluorene units emitted light at 435 nm, while the one bearing thiophene moieties emitted blue light at 470 nm in solution.

On the other hand TiO_2 is an extensively studied and technologically important wide band gap semiconductor widely used in various applications as for example in batteries or electron injection solar cells [14–16]. In dependence on the application of TiO_2, the conditions of the synthesis which can modify the surface properties, phase, and morphology of TiO_2 are very important. TiO_2 can exist in three forms such as anatase, brookite or rutile [14–16]. The anatase phase of TiO_2 is photochemically more active compared with the brookite and the thermodynamically stable rutile form. For solar cell applications, TiO_2 typically serves as the favored n-type semiconductor in the form of an interpenetrating, three dimensionally continuous percolating matrix with the voids filled with the electrolyte or a p-type semiconductor [14–16]. Anatase phase of TiO_2, has a band gap (Eg) at 3.2 eV and absorbs light in the UV region of the solar spectrum [14–16].

Among the polyazomethine devices with TiO_2, only dendrimers with triphenylamine core were used as an active layer of Dye Sensitized Solar Cells (DSSC) [17,18]. In the DSSC, the bulk of the semiconductor is used solely for charge transport, the photoelectrons are provided from a separate photosensitive dye. Charge separation occurs at the surfaces between the dye, semiconductor and electrolyte [19]. Phenyloazomethine dendrimer with triarylamine core and two carbazolo dendrimers contained third generation of cyclic phenyloazomethine were used as organic part of DSSC, where dye was coated with dendrimer [17,18]. Current–voltage measurements of device with such architecture as FTO/TiO_2/dendrimer/Pt, where FTO it is fluorine-doped tin oxide glass were investigated. The suppression of the back electron transfer by a modified interface improves the open-circuit voltage. Authors of [17,18] claimed that proposed dendrimers were attended as charge separators in organic active layer of solar cells.

In order to investigate the influence of triphenylamine for optoelectrical applications of polyazomethines we synthesized branched polyazomethines with different feed molar ratio. Additionally, compounds end-capped with triphenylamine or naphthylamine were also investigated. The structural characterization was performed by NMR, FTIR, GPC and elemental analysis completed with optical and electrical investigations. In accordance with the best our knowledge the optical and electrical properties of the branched polyazomethines undoped and doped with iodine presented in this paper were not investigated so far.

2. Experimental

2.1. Materials

All chemicals were used without any purification as received from Aldrich.

2.2. Characterization techniques

The obtained polymers were characterised by the following techniques: ^{1}H NMR (Varian Innova 600 Spectrometer, $CDCl_3$ solvent against TMS as an internal reference), and FTIR. Infrared spectra were acquired on a DIGILAB FTS-40A Fourier transform infrared spectrometer in the range of 4000–400 cm^{-1} at a resolution of 2 cm^{-1} and for an accumulated 32 scans. Polymers were analyzed onto potassium bromide plates and as pellets in potassium bromide (ν – stretching vibrations, δ – in plane deformation, γ – out-of-plane deformation, ω – wagging vibrations, as – asymmetric, s – symmetric, Ph – phenyl, sh – shoulder). Tg of the synthesized compounds was determined by differential scanning calorimetry (DSC) on a TA-DSC 2010 apparatus using sealed aluminium pans under nitrogen atmosphere. UV–vis absorption spectra in solution and in film on the glass were recorded using a Hewlett–Packard 8452A spectrophotometer whereas the photoluminescence of chloroform solution spectra were registered on a Hitachi F-2500 (resolution 2 nm). Molar masses (weight average molar mass, Mw and number average molar mass, Mn) and molar mass dispersity (MD, Mw/Mn) of samples were determined by GPC experiments in chloroform (GPC solvent, stabilized with amylene, purity 99.98%, Fischer Chemical) at 35 °C with an eluent flow rate of 1 mL/min, using PLeg 3 μm MIXED-E column (Polymer Laboratories). An isocratic pump (Spectra Physics 8800) as the solvent delivery system and differential refractive index detector stabilized to a temperature of 35 °C (Shodex SE 61). A volume of 10 μL of about 3% w/v sample solution in chloroform was injected. Polystyrene standards (Calibration Kit S-M-10, Polymer Laboratories) with narrow molar mass dispersity were used to generate a universal calibration curve. Samples were calculated using OmniSEC 4.1 (Viscotek) software. Current–voltage characteristics were detected using electrometer Keithey 6517A. The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were carried out in a three-electrode electrochemical cell. Platinum disc (diameter 1.0 mm) and platinum wire were used as working and counter electrodes, respectively, and Ag wire as a pseudo-reference, which potential was monitored versus ferrocene. In all experiments the sample concentration was 0.5 mmol/l and a 0.2 M solution of Bu_4NPF_6 (Aldrich 98% purity) in dry dichloromethane was used as a supporting electrolyte solution. Cyclic voltammetry measurements were performed at a scan rate of 100 mV/s at room temperature. All solutions have been deaerated with Ar gas prior to the experiments. The surface morphology investigations of the TiO_2 and selected devices were performed in air using a commercial Innova AFM system from Veeco Company. Measurements were done in Tapping Mode and Phase Imaging. Also Local Contrast data processing was made. Typical cantilever (about 40 N/m and <10 nm tip curvature) was used.

2.3. Model compounds synthesis

M1: 4-Formyltriphenylamine (0.50 mmol, 0.136 g), 3,3′-dimethoxybenzidine (DMB) (0.25 mmol, 0.061 g), p-toluenesulfonic acid (PTS, 0.004 g) and 5 mL of dichloroethane were introduced into a 20-ml, two-necked, round-bottomed flask equipped with a magnetic stirrer, a reflux condenser and a nitrogen inlet. The mixture was stirred and heated at 80 °C during 6 h in an oil bath. Then solvent was evaporated and the solid residue