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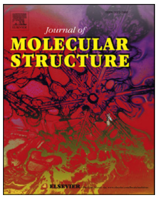

Azomethine diimides end-capped with anthracene moieties: Experimental and theoretical investigations

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ABSTRACT

New arylene bisimide derivatives containing imine linkages and anthracene units were synthesized. Azomethine diimides were prepared via condensation reaction of 9-anthracenecarboxaldehyde and diamines with phthalic diimide or naphthalene diimide core and Schiff base linkers. They were characterized by FTIR spectroscopy, elemental analysis and mass spectrometry (MALDI-TOF-MS). The synthesized compounds exhibited high resistance against thermal decomposition up to 400 °C. Investigated compounds are electrochemically active and undergo reversible electrochemical reduction and irreversible oxidation processes as was found in cyclic voltammetry studies. The photoluminescence measurements of synthesized compounds in solid state as thin film on glass substrate revealed their ability to emission of the blue light with quantum yield efficiency about 2%. The electronic structure and spectroscopic properties of prepared azomethine diimides were also calculated by the density functional theory (DFT). The electrical properties of the diimide derivatives were preliminary investigated by current–voltage measurements.

1. Introduction

Since the first demonstration of light-emitting diodes (OLEDs) and photovoltaic (PV) devices based on organic materials about 30 years ago [1,2], the development of organic conjugated systems for (opto)electronic devices is a challenging topic of current research. Two classes of organic semiconductors are known, that is, low molecular weight compounds and polymers. Small molecular weight compounds offer significant potential in the applications due to well-defined structures, easier purification and more easily controllable properties in comparison to polymers [3]. In the rich chemistry of conjugated systems arylene imides-based materials and the compounds bearing Schiff-base linkers are interesting semiconductors [4,5]. Compounds with imide structure possess excellent thermal stability, good chemical and oxidative resistance and exhibit n-type semiconducting properties [6]. On the second hand, the molecules with imine linkages are isoelectronic to their vinylene counterparts and exhibited hole-transporting properties, thus they seem to be suitable alternatives to conventional p-type materials [5]. Based on these findings and the fact that compounds consisting of both electron-donating and electron accepting (D/A) moieties are desired for optoelectronics [7,8] we designed and synthesized family azomethine diimides [9–16]. In such type of compounds D-A system is created by introduction of imine bonds into the structure of imide compound. Continuing our effort in the synthesis of compounds for potential applications in organic optoelectronics [17–20] in this work we present new azomethine diimides end-capped with anthracene units. Anthracene is first organic substance in which electroluminescence was observed [21], from that time there were many researches on using anthracene-containing materials for optoelectronics [22–32]. Either polymeric [31,33,34] and low molecular [21,26,30] anthracene derivatives were investigated, ability to emit blue light is one of their most interesting features [23,26,27]. In the present paper photophysical and electrochemical properties of new anthracene-containing azomethine diimides were studied theoretically by density functional theory (DFT) and experimentally by using UV–vis, photoluminescence (PL) spectroscopies and cyclic

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voltammetry (CV). Moreover, their thermal properties were evaluated by different scanning calorimetry (DSC) and by thermogravimetrical analysis (TGA). Moreover a preliminary study of current–voltage characteristic of devices based on these compounds was performed. The prepared compounds possess various the chemical structure of both the diimide core and the moieties between the diimide rings and imine linkages.

2. Experimental section

2.1. Materials

9-Anthracenecarboxaldehyde, benzene-1,2,4,5-tetracarboxylic dianhydride, 1,4,5,8-naphthalenetetracarboxylic dianhydride, 2,3,5,6-tetramethyl-1,4-phenylenediamine, 1,4-naphtalenediimide, N,N-dimethylacetamide (DMA), trifluoroacetic acid (TFA), N-methyl-2-pyrrolidinone (NMP), chloroform were purchased from Aldrich Chemical Co and used as received. N,N′-bis(4-amino-2,3,5,6-tetramethylphenyl)phtalene-1,2,4,5-dicarboximide (DAPhDI), N,N′-bis(5-aminonaphtalen)phtalene-1,2,4,5-dicarboximide (DAPhDI-2), N,N′-bis(4-amino-2,3,5,6-tetramethylphenyl)naphthalene-1,4,5,8-dicarboxyimide (DANDI), N,N′-bis(5-aminonaphtalen)naphthalene-1,4,5,8-dicarboxyimide (DANDI-2) were synthesized according the procedure describe in our previous work [3,10].

2.2. Synthesis of azomethinediimides: general procedure

9-Anthracenecarboxaldehyde (1 mmol), diamine (DAPhDI, DAPhDI-2, DANDI and DANDI-2) (0.5 mmol) and 0.2 ml of trifluoroacetic acid were added to 4 ml of DMA and heated (160 °C) under argon atmosphere. After 16 h, the mixture was filtrated. The precipitant was washed several times with hot methanol and dried at 100 °C in vacuum.

AzDI-1: FTIR (KBr, cm^{-1}) ν: 1773, 1723 (C=O imide stretch), 1632 (CH=N), 1354 (C–N stretch), 732 (imide ring deformation). Anal. Calcd. for $C_{60}H_{46}N_4O_4$ (887.03) C: 81.24%; H: 5.23%; N: 6.32%; Found C: 82.44%; H: 5.61%; N: 5.69%. MALDI-TOF-MS: 886.6 g/mol. Yield 52%.

AzDI-2: FTIR (KBr, cm^{-1}) ν: 1775, 1725 (C=O imide stretch), 1624 (CH=N), 1354 (C–N stretch), 741 (imide ring deformation). Anal. Calcd. for $C_{60}H_{34}N_4O_4$ (874.94) C: 82.37%; H: 3.92%; N: 6.40%; Found C: 82.82%; H: 4.19%; N: 6.82%. MALDI-TOF-MS: 874.7 g/mol. Yield (50%).

AzDI-3: FTIR (KBr, cm^{-1}) ν: 1712, 1675 (C=O imide stretch), 1622 (CH=N), 1340 (C–N stretch), 766 (imide ring deformation). Anal. Calcd. for $C_{64}H_{48}N_4O_4$ (937.09) C: 82.03%; H: 5.16%; N: 5.98%; Found C: 81.50%; H: 4.17%; N:5.72%. MALDI-TOF-MS: 937.09 g/mol. Yield 50%.

AzDI-4: FTIR (KBr, cm^{-1}) ν: 1712, 1675 (C=O imide stretch), 1625 (CH=N), 1337 (C–N stretch), 770 (imide ring deformation). Anal. Calcd. for $C_{64}H_{36}N_4O_4$ (924.995); Found C: 83.10%; H: 3.92%; N: 6.06% Found C: 83.82%; H: 3.62%; N: 6.64%. MALDI-TOF-MS: 924.7 g/mol. Yield 51%.

2.3. Measurements

Infrared spectra were acquired on Perkin Elmer Spectrum One and samples were analyzed as KBr pressed pellets were performed. Elemental analysis was determined by a Vario EL III Elementar apparatus. UV–Vis spectra were measured using a JASCO V570 UV–Vis–NIR spectrometer. The photoluminescence were recorded with Hitachi F-2500 spectrometer. Differential scanning calorimetry (DSC) measurements were carried out using a Du Pont 1090B apparatus with a heating rate of 20°C/min under nitrogen. The thermal stability of polymers was evaluated with a PerkinElmer TG Pyris-1 thermal analyzer at 10 °C/min in a stream of nitrogen (20 cm^3/min^1) in the temperature range 25–800 °C. Mass spectra were recorded on a Shimadzu AXIMA Performance MALDI–TOF mass spectrometer operated in linear mode. The laser power was optimized to obtain a good signal-to-noise ratio after averaging 250 single-shot spectra. Samples were dispersed in chloroform ($CHCl_3$) and placed in an ultrasonic cleaner for 15 min. Afterwards, 1,5 μL of the sample solution was spotted on a stainless-steel target plate and air dried for several minutes at room temperature. Data were collected in continuum mode with 250 profiles collected by laser firing and 5 shots accumulated into one profile. Data were obtained and analyzed using Shimadzu Biotech Launchpad program. Electrochemical behavior of the compounds was tested using ATLAS 0531 Electrochemical Unit & Impedance Analyzer potentiostat. 0.2 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 Aldrich, 99%) in acetonitrile (Aldrich, HPLC grade) was used as the supporting electrolyte. The solution was purged with argon. The oxidation and reduction potentials of film deposited on a ITO disk were measured using a Pt wire and a quasi-Ag/AgCl electrode as a counter electrode and a reference electrode, respectively. Ferrocene (Fc) was used as the internal standard for potentials calculations. The frontier molecular orbitals (HOMO and LUMO) levels were estimated with assumption that the absolute energy level of Fc/Fc^+ is equal to −5.1 eV to vacuum [7]. Ellipsometer SENTECH SE 850 E was applied for the film thickness measurements. The current–voltage measurements were carried out using a Keithley 6517A source-measure unit.

2.4. Theoretical calculation (DFT)

The calculations were carried out using the Gaussian09 [35] program. The DFT/B3LYP [36] method was used for the geometry optimization and electronic structure determination. The calculations were performed with use of 6–31g(d,p) basis set to describe the molecule atoms. GaussSum 3.0 [37] was used to calculate groups (i.e. those molecule fragments such as antracene, phthalic diimide in the case of **AzDI-1** and **AzDI-2;** naphthalene diimide for **AzDI-3** and **AzDI-4**, −HC=N− and 1,2,4,5-tetramethylbenzene) contribution to the molecular orbitals. Chemcraft program package (http://www.chemcraftprog.com) was utilized for molecular orbital plots generation. CIS(D) (single excitation configuration interaction with doubles correction) method was applied for calculations of the electronic transitions [38].

2.5. Film preparation

Films were prepared by thermal evaporation of compounds at 350 °C in vacuum (5×10^{-5} tor).

2.6. Device preparation

Devices with configuration: ITO/PEDOT:PSS/compound/Al were prepared. For devices fabrication OSILLA substrates with pixilated ITO anodes, cleaned sequentially with detergent, deionized water, 10% NaOH solution, water and isopropanol in an ultrasonic bath were applied. ITO layer was covered with PEDOT:PSS thin film (40 nm) by spin coating at 5000 rpm for 60 s and annealed for 15 min at 130 °C. Active layer was vacuum deposited (vacuum 5×10^{-5} tor, 20 min at 350 °C). An aluminum cathode (about 100 nm) was vacuum-deposited.

3. Results and discussion

Azomethinediimides reported in this work were prepared by