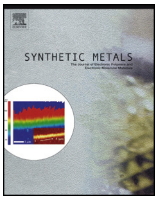
Synthetic Metals 175 (2013) 146–154

Contents lists available at SciVerse ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



New azomethine-phthalic diimides: Synthesis and thermal, optical and electrochemical characterization

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ARTICLE INFO

Article history:
Received 21 February 2013
Received in revised form 8 May 2013
Accepted 15 May 2013
Available online 11 June 2013

Keywords:
Diimides
Photoluminescence
Thermotropic liquid crystals
Electrochemistry

ABSTRACT

A new diamine with phthalic diimide moiety, i.e. N,N′-bis(4-amino-2,3,5,6-tetramethylphenyl)phthalene-1,4-dicarboxyimide was synthesized and applied for condensation with 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy)benzaldehyde and 4-octadecyloxybenzaldehyde, which resulted in two new azomethine-phthalic diimides (AZ-PDIs). Thermal, optical and electrochemical properties of AZ-PDIs were discussed in relation to their analogous containing instead of five-membered six-membered imide rings (AZ-NDIs) described in our previous work. The phase behavior of AZ-PDIs examined by differential scanning calorimetry (DSC) and polarized optical microscopy (POM) confirms their liquid crystalline properties in wide range of temperatures. AZ-PDIs do not show decomposition below 400 °C as was found based on thermogravimetric analyses (TGA). Optical properties of the prepared compounds were investigated by UV–vis and photoluminescence (PL) measurements. Azomethine-phthalic diimides emitted blue light with emission maximum (λ_{em}) at ca. 446–492 nm contrary to azomethine-naphthalene diimides which emitted green light and λ_{em} was at 536 and 540 nm. The obtained compounds are electrochemically active and undergo reversible reduction and oxidation as evidenced by differential pulse voltammetry (DPV). The azomethine-phthalic diimides exhibited low electrochemical band gap ca. 1.68 eV being promising for optoelectronic applications.

1. Introduction

Photo-and electroactive organic materials both low molecular weight compounds and polymers have been the subject of recent attention because of potential applications in electronic and optoelectronic devices. The important advantages of organic materials are light-weight, low processing cost, solution processability and tunability of their properties by structure modification [1,2]. In particular, there is interest in conjugated systems called organic semiconductors both from the basic research and application standpoint. Special attention is paid on self-assemble materials with a high degree of intra/intermolecular order [3,4]. Self-organization may provide some interesting features, such as improved charge transfer abilities [5]. Among the self-assemble systems, low and high molecular weight liquid crystals (LCs) are particularly interesting owing to their ability to form large aligned domains, which enable the formation of well-ordered thin films [3]. Thermotropic liquid crystals (TLC) have received great attention due to their practical applications in organic light-emitting devices [6,7], organic field-effect transistors [8,9] and photovoltaic cells [10,11] and significant efforts have been centered on the synthesis of new TLC compounds [9]. Among many designed and synthesized organic materials, compounds with imide groups are particularly interesting as promising both liquid crystalline materials and organic semiconductors. Aromatic imide groups are almost planar, rigid, polar and thermostable, and therefore should reveal mesogenic character [12]. On the other hand, compounds consisting of electron deficient aromatic imide rings are particularly interesting as organic n-type semiconductors. Since the report of naphthalenetetracarboxylic diimides as air stable n-channel materials, a large number of either naphthalene or perylene tetracarboxylic diimides has been synthesized and investigated [13,14]. Such imides contain six-membered imide rings. Other kind of imides are compounds with five-membered imide rings, that are, tetracarboxylic diimides. It is quite surprising that they are only occasionally investigated as semiconductors. To the best of our knowledge, only three articles described such investigations [3,15,16]. Although liquid crystalline five-membered imides have been described in the literature, especially compounds with ester group [17–21], they have not been investigated as semiconductors except for Dingemans et al. one article [16] and one our work [21].

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http://dx.doi.org/10.1016/j.synthmet.2013.05.017

Another promising type of compounds which can combine TLC and semiconducting properties are azomethines (AZs), which are also known as imines and Schiff bases. Azomethines due to presence of imine bond (N═CH) are isoelectronic to their carbon analogs, making them suitable alternatives to conventional conjugated materials and can be exploited for various applications [22–24]. These compounds are predominately p-type materials in contrast to diimides, which exhibit n-type behavior and TLC azomethines were investigated as hole-transporting materials [25–29]. Inspired by the findings described above we have undertaken a preparation and investigation of low molecular weight compounds and polymers comprised diimide and imine units which can be considered as a new type of diimides. Although many diimides are known, new diimides are enduring to appear as researches continue to conduct fundamental study on chemical–structure relationship and search for compounds with unique combination of properties for special applications. The introduction of imine bonds into the structure of imide compounds allows obtaining donor–acceptor system useful for various optoelectronic applications. These compounds constitute a promising family of materials whose properties can be explored in various types of devices. In our previous work we described TLC azomethine-naphthalene diimides [29].

This paper is devoted to the synthesis of a new thermotropic azomethine-phthalic diimides and studies their chosen physical properties such as: thermal (DSC, POM, TGA), optical (UV–vis, PL) and electrochemical (DPV). The properties of the obtained compounds and their analogs, i.e. azomethine-naphthalene diimides synthesized earlier in our laboratory [29] were compared. Moreover, photoluminescence properties and thermal stability of described previously azomethine-naphthalene diimides [29] were investigated. Two aldehydes with long flexible chains, that is, 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy)benzaldehyde and 4-octadecyloxybenzaldehyde, were chosen for the preparation of the compounds. These aldehydes were also used in the synthesis of the symmetrical TLC azomethine-naphthalene diimides [29]. The fluorinated aldehyde was chosen because of the important role of fluorine substituents in tailoring the physical properties of compounds. The introduction of fluorine atoms modifies such physical properties as phase transition temperatures, dielectric properties, birefringence and elastic constants [30]. On the other hand, the presence of fluorine atoms in alkyl chains enhances the thermal stability of LC mesophases and influences the mesophase morphologies. The stabilization of smectic mesophases with an increasing number of fluorine atoms in fluoroalkylated imines was observed [30].

2. Experimental

2.1. Materials

Benzene-1,2,4,5-tetracarboxylic dianhydride (pyromellitic dianhydride, PMDA), 2,3,5,6-tetramethyl-1,4-phenylenediamine, N,N-dimethylacetamide (DMA), N,N-dimethylformamide (DMF) and toluene-4-sulfonic acid trifluoroacetic acid were purchased from Aldrich Chemical Co. 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy)benzaldehyde and 4-octadecyloxybenzaldehyde were supplied from Fluka.

2.2. Synthesis of N,N′-bis(4-amino-2,3,5,6-tetramethylphenyl)phtalene-1,2,4,5-dicarboximide (DAPDI)

PMDA (0.6544 g, 3 mmol) and 2,3,5,6-tetramethyl-1,4-phenylenediamine (2.4637 g, 15 mmol) were added to 30 ml DMF and refluxed under argon atmosphere. After 3 h the mixture was cooled to room temperature and poured into 150 ml water. The diamine precipitate was collected by filtration, washed with hot methanol and dried. Yield: 60%, beige solid.

^{1}H NMR (DMSO-d$_6$, δ, ppm): 1.90 (s, CH$_3$, 12H), 2.06 (s, CH$_3$, 12H), 4.81 (s, NH$_2$, 4H), 8.41 (s, 2H). FTIR (KBr, cm^{-1}): 3481, 3391 (—NH$_2$ stretch), 2986–2859 (C—H aliphatic), 1774, 1721 (C═O imide stretch), 1633 (—NH$_2$ deformation), 1317 (C—N stretch), 732 (imide ring deformation).

2.3. Synthesis of azomethine-phthalic diimides (AZ-PDIs)

Diamine DAPDI (0.1276 g, 0.25 mmol), aldehyde (4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy)benzaldehyde (0.2910 g, 0.5 mmol); or 4-octadecyloxybenzaldehyde (0.1875 g, 0.5 mmol) and a few drops of trifluoroacetic acid were added to 5 ml DMA and heated (160 °C) under argon atmosphere. After 16 h the mixture was cooled to room temperature. The precipitate was collected by filtration, washed with hot methanol and dried.

DAPDI condensed with 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy)benzaldehyde gave compound AZ-PDI-I and DAPDI condensed with 4-octadecyloxybenzaldehyde resulted in compound AZ-PDI-II.

AZ-PDI-I: yield: 37%, yellow solid. ^{1}H NMR (CDCl$_3$, δ, ppm): 2.08 (d, CH$_3$—Ar, 24H), 2.16 (m, CH$_2$, 4H), 2.35 (m, CH$_2$, 4H), 4.14 (t, CH$_2$—O, 4H), 7.02 (d, 4H), 7.89 (d, 4H), 8.10 (s, CH═N, 2H), 8.55 (s, 2H). FTIR (KBr, cm^{-1}): 2950–2868 (C—H aliphatic), 1778, 1726 (C═O imide stretch), 1638 (CH═N), 1606 (C═C stretching deformations in the phenyl ring), 1350 (C—N stretch), 732 (imide ring deformation). Anal. Calcd. for ($C_{66}H_{48}N_4O_6F_{34}$) (1639.06): C 48.36, H 2.95, N 3.42; Found: C 49.13, H 2.43, N 3.67.

AZ-PDI-II: Yield: 61%, yellow solid. ^{1}H NMR (CDCl$_3$, δ, ppm): 0.87 (t, CH$_3$, 6H), 1.26 (m, CH$_2$, 52H), 1.48 (m, CH$_2$, 8H), 1.83 (quint, CH$_2$, 4H), 2.07 (d, CH$_3$—Ar, 24H), 4.04 (t, CH$_2$—O, 4H), 7.01 (d, 4H), 7.87 (d, 4H), 8.09 (s, CH═N, 2H), 8.54 (s, 2H). FTIR (KBr, cm^{-1}): 2921, 2852 (C—H aliphatic), 1778, 1723 (C═O imide stretch), 1638 (CH═N), 1605 (C═C stretching deformations in the phenyl ring), 1352 (C—N stretch), 732 (imide ring deformation). Anal. Calcd. for ($C_{80}H_{110}N_4O_6$) (1223.75): C 78.52, H 9.06, N 4.58; found: C 78.36, H 9.01, N 5.22.

2.4. Characterization

FTIR spectra were recorded on a 560 MAGNA-IR NICOLET spectrometer using KBr pellets. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker AC 400 MHz spectrometer using DMSO-d$_6$ or chloroform (CDCl$_3$) as solvents and TMS as the internal standard. Elemental analysis data were obtained using a Perkin Elmer 2400 apparatus. Differential scanning calorimetry (DSC) was performed with a TA-DSC 2010 apparatus (TA Instruments, Newcastle, DE, USA) under nitrogen using aluminum sample pans. Thermogravimetric analyses (TGA) were performed on a Perkin Elmer apparatus at heating rate of 10 °C/min under nitrogen. The textures of the liquid-crystalline phases were observed with a polarized optical microscope (POM) Zeiss (Opton-Axioplan) equipped with a Nikon Coolpix 4500 color digital camera and Mettler FP82 hot plate with Mettler FP80 temperature controller. UV–vis absorption spectra were recorded using a Lambda Bio 40 Perkin Elmer spectrophotometer. The PL spectra were obtained on a VARIAN Cary Eclipse Fluorescence Spectrophotometer. Electrochemical measurements were carried out using Eco Chemie Autolab PGSTAT128n potentiostat, using platinum wire (diam. 1 mm), platinum coil and silver wire as working, auxiliary and reference electrode, respectively. Potentials are referenced with respect to ferrocene (Fc), which was used as the internal standard.