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New thermotropic symmetrical and unsymmetrical azomethine with azobenzene unit and fluorinated alkyl chain: Synthesis and characterization

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ABSTRACT

A new thermotropic liquid crystals containing azobenzene unit and imine linkages were synthesized via condensation of 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy)benzaldehyde with 4-aminoazobenzene (AzoAz-1) and 4,4′-diaminoazobenzene (AzoAz-2). The structures of compounds were characterized by means of NMR, FTIR spectroscopy and elemental analysis; the results show an agreement with the proposed structure. The mesomorphic behavior of the unsymmetrical AzoAz-1 and symmetrical AzoAz-2 azobenzeneimines was investigated via differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). Based on the POM and DSC measurements AzoAz-1 exhibited smectic phases (SmX, SmA), while AzoAz-2 showed smectic (SmX1, SmX2, SmA) and nematic (N) mesophases. Optical properties of the azobenzeneimines were tested by UV–vis and photoluminescence (PL) spectroscopy in various solvents. Preliminary investigations of electrical properties of the new compounds were carried out by current–voltage (I–V) measurements performed on ITO/compound/Al device.

1. Introduction

Azobenzene, with its two phenyl rings separated by an azo bond, acts as the parent structure for a broad class of photoresponsive chromophores which have received much attention in both fundamental and applied research areas [1,2]. Azobenzene groups are known to exist in two isomeric states, a thermodynamically stable trans and a metastable cis form. When irradiated with light of an appropriate wavelength, they undergo a multiple reversible trans↔cis photoisomerization process, which leads to noticeable changes in the physical properties of material [3]. Thus, azobenzene containing materials have attracted considerable attention owing to their potential application in optical data storage, optical image processing, dynamic holography, nonlinear optical (NLO) materials, waveguide switches [4–7]. It should be stressed that, besides optical manipulations, some reports have demonstrated the potential of azobenzene molecules to function as molecular switches at the nanoscale level and electric memories based on voltage-induced electric bistability of azopolymers [8]. On the other hand, thermotropic liquid crystals (TLC) are fascinating materials which offer a variety of unique properties and have received great attention due to their practical applications and synthesis of new TLC compounds are one of the important areas for material research community [9–11]. Among many liquid crystals (LC) compounds of special interest are those containing mesogens based on azobenzene moiety and various types of such LC chromophores have been reported [4,12–16]. The azobenzene derivatives which contain imine (–C═N–) bond seem to be interesting kind of LC compounds, which have hardly been studied. The imine bond is usually built into the molecular structure to increase the length and polarisability anisotropy of the compound and consequently enhance liquid crystal phase stability [17]. Compounds with imine linkages, so called azomethines or Schiff bases are one of the oldest groups of liquid crystals and show rich polymorphism [18,19]. As far as we are aware, only a few papers are devoted to low molecular weight LC compounds with imine linkage and azobenzene unit [20–23]. Our previous report [24] showed the liquid crystal iminie obtained from 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy)benzaldehyde exhibited more enantiotropic transitions with narrow temperature range, smaller value of energy band gap then compound prepared from aldehyde without F atoms. Fluorine substitution is an important tool to modify materials by chemical design. It was found that fluorinated chains introduced into LC compounds improve solubility, decrease phase transition temperatures, enhance the thermal stability of the liquid crystalline phases and modify the mesophase morphologies in comparison with the same compound with aliphatic chains [17,25].

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Inspired by the findings described above and continuing our effort in synthesis of new azobenzene functionalized materials [26–29] we have undertaken a preparation and investigation of a new LC compounds, that is azomethine with azobenzene moiety (abbreviated hereinafter as AzoAz).

The objective of the present work was to synthesize new thermotropic azoimines, and study their chosen properties. In this article we present the physicochemical (NMR, FTIR), thermal (DSC, POM), optical (UV–vis, photoluminescence) and electrical (current–voltage) characterizations of the new thermotropic liquid crystal AzoAz.

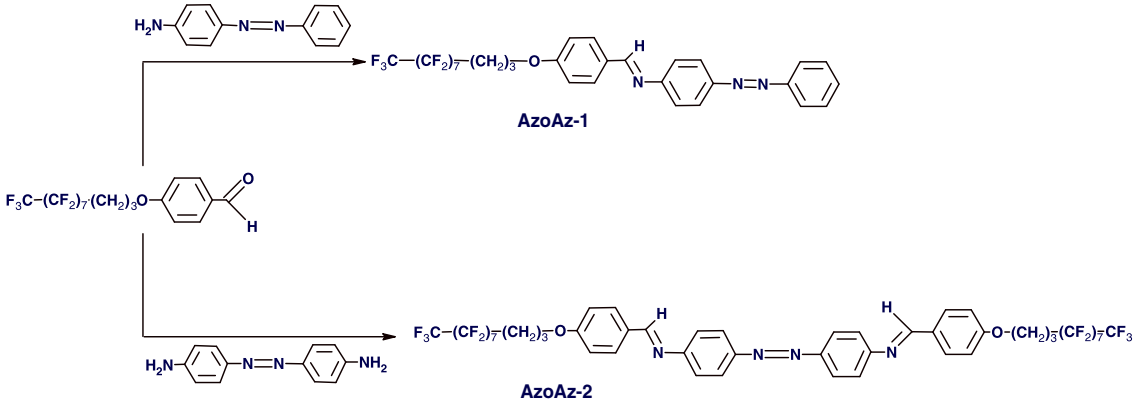

Fig. 1. Synthetic route and chemical structure of the synthesized azobenzeneimines.

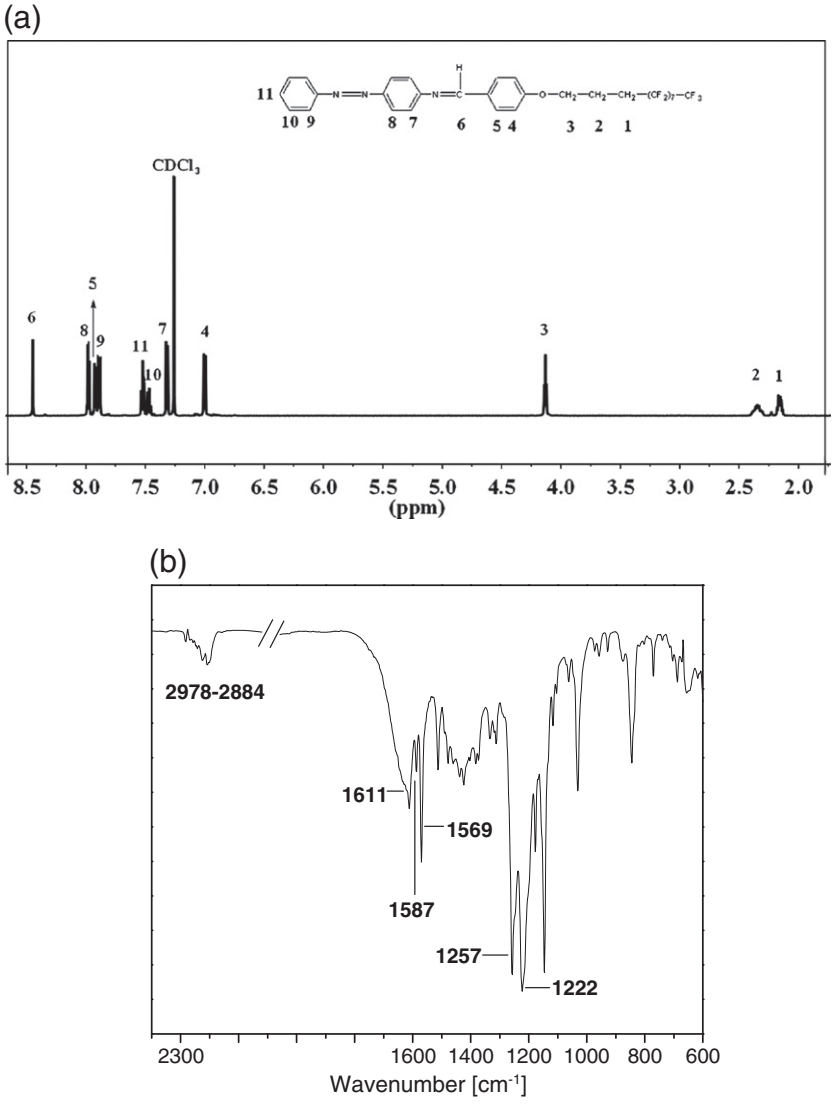

Fig. 2. ^{1}H NMR (a) and FTIR (b) spectra of AzoAz-1.