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Thermotropic and opto(electrical) properties of liquid crystalline imine with two fluorinated chains

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ABSTRACT

The optical, electrical and thermal properties of unsymmetrical imine with two fluorinated chains are described. The structure of imine was characterized by means of ^{1}H, ^{13}C NMR spectroscopy and elemental analyses and the results show an agreement with the proposed structure. The wide-angle X-ray diffraction [WAXD(T)] technique in different temperatures was used to probe the structural properties of the azomethine. Mesomorphic behaviour was investigated via differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) studies. Additionally, the mesomorphic behaviour of the azomethine presented in this work was compared with other azomethines. The absorption (UV-vis), photoluminescence (PL) and thermoluminescence (TL) features of the compound are documented. The sample was irradiated with a test dose of 2 Gy Co-60 gamma rays. Current–voltage (I–V) measurements were performed on an ITO/Az/Al device in the dark and during irradiation with light (under illumination of 1000 W/m^2).

1. Introduction

Presently, liquid crystal (LC) compounds are materials of marvelous technological (cell phones, laptop displays, digital watches, calculators) and scientific importance, thanks to their optical and electrical properties. Among the huge group of LC compounds with fluoro substituents or chain fluorination, an imines with F substituents or fluorinated chain are the subject of the investigation as the mesogenic materials [1–12]. Unsymmetrical imines with perfluorinated chain were investigated by Bilgin-Eran et al. [7] and Iwan et al. [12]. The authors in [8] found that the thermal behavior of the semiperfluorinated imines depends on the number of chain, the substitution pattern and the number of fluorine atoms in the fluoroalkyl chains. Along with increasing the number of F atoms in the fluoroalkyl chains, the stabilization of smectic and columnar mesophases was observed [7]. We recently reported the synthesis, characterization and mesomorphic properties of unsymmetrical imines based on 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy)benzaldehyde [12]. Enantiotropic smectic phases were observed for all the systems studied.

The azomethine bond (–HC = N–) is usually incorporated into the molecular structure to increase the length and polarisability anisotropy of the compound core and consequently enhance liquid crystal phase stability. Moreover, azomethines are a very interesting class of organic compounds in the investigations of their liquid crystal properties from the point of view of their rich polymorphism [7–9,12–16].The fluoro substituent in organic compounds influences polar and steric effects and confers stability on fluoro substituted compounds by the great strength of the C–F bond [1]. Our previous report [12] showed that the mesomorphic behavior of the azomethines obtained from 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy) benzaldehyde and different amines strongly influence the kind of used amine. For this reason, in this paper, we would like to show the influence of fluoroalkyl segments coming from aldehyde and amine on the mesomorphic and opto(electrical) properties of the strongly polar azomethine.

In this paper, we report on the synthesis, mesomorphic behavior and the electrical and photophysical properties of the azomethine shown in Fig. 1a. The rationale for this new chemical structure is given as follows: (i) the azomethine unit was selected because azomethines exhibited semiconducting properties, good thermal stability and thermotropic behavior [17] and (ii) the terminal fluorinated chains improve solubility, decrease phase transition temperatures, enhance the thermal stability of the LC mesophases, modify the mesophase morphologies in comparison with the same compound with aliphatic chains and influence the electronic properties of the compounds [1].

Studies reported here investigate an unsymmetrical rod-shaped imine with a long alkoxysemiperfluorinated chain ($–O–(CH_2)_3–(CF_2)_7–CF_3$) derived from the aldehyde and heptadecafluorooctyl chain ($–(CF_2)_8–CF_3$) derived from amine. The liquid crystal properties of the imine were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The structural characterization was performed by proton and carbon NMR characteristics completed via X-ray diffraction measurements and optical and electrical investigations. In accordance with the best of our knowledge, the LC behavior, as well as the thermoluminescence and electrical properties of the imine with two

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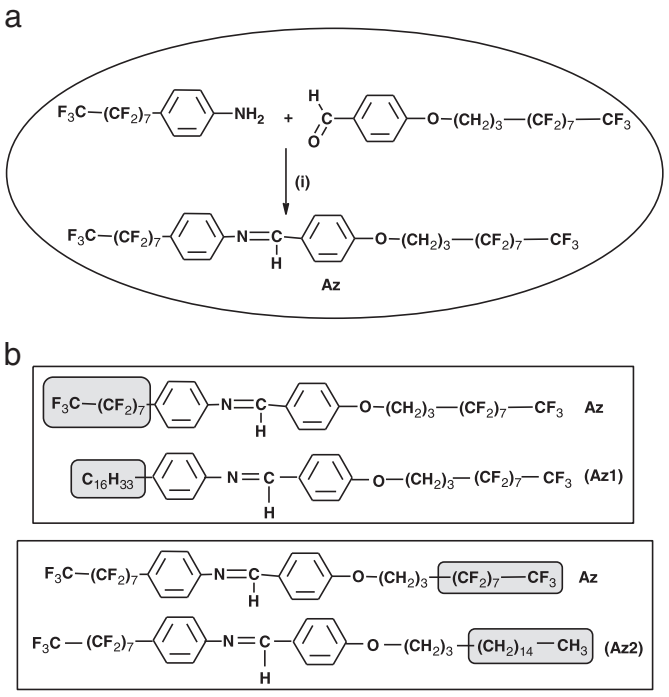

Fig. 1. (a) Synthetic route and chemical structure of the synthesized azomethine **Az**: (i) DMA, PTS, 160 C, 10 h. (b) chemical structure of the selected azomethines with different type of side groups.

long perfluorinated chains, presented in this paper have not been investigated so far.

2. Experimental section

2.1. Materials

All chemicals were used without any purification.

2.2. Characterisation techniques

The synthesized compound was characterized by proton and carbon NMR spectroscopy and elemental analysis. NMR was recorded on a Bruker AC 200 MHz Chloroform-*d* ($CDCl_3$) containing TMS as an internal standard was used as the solvent. Elemental analyses (C, H, and N) were carried out by the 240C Perkin–Elmer analyzer.

The phase transitions and mesogenicity were studied through differential scanning calorimetry (DSC) and polarizing microscope observations (POM). DSC was measured on a TA-DSC 2010 apparatus using sealed aluminium pans under a nitrogen atmosphere at heating/cooling cycles. X-ray diffraction patterns were recorded using powder on a pulveraceous diffractometer Dron–2. Co radiation filtrated by Fe was applied.

Thermoluminecent (TL) measurements were realized using the RA'94 TL reader/analyzer. It is equipped with a platinum planchet heater and a photomultiplier with a bialkali photocathode. The sample was irradiated with a test dose of 2 Gy Co-60 gamma rays. Measurements were performed with a linear heating ramp at a rate of 4 K/s up to 475 K using a green filter.

UV-vis absorption spectrum was recorded on a JASCO V-670 spectrophotometer. A thin film was prepared from the chloroform solution of **Az** and was spread on quartz using a spin-coating method. Quartz substrates were purified using an ultrasonic washer with an organic solvent (chloroform) for1 h. After that, substructures were cleaned using toluene, isopropanol and acetone. Characteristic parameters related with speed (880 turns/min) and time (10 s) rotation were implemented to the spin-coating equipment.

Photoluminescence THF solution spectrum was carried out on a Jobin–Yvon HR 550 monochromator equipped with a CCD silicon detector (325-nm excitation line).

Current–voltage (I–V) characteristics were detected using the Keithley 6517B electrometer.

2.3. Synthetic procedure of the imine Az

A mixture of 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy)benzaldehyde (1.0 mmol) and 4-(heptadecafluorooctyl) aniline (1.3 mmol) in N,N-dimethylacetamide (DMA) solution, with the presence of *p*-toluenesulfonic acid (PTS; 0.06 g) was refluxed with stirring for 10 h. The reaction was conducted in an argon atmosphere. After cooling, the mixture was precipitated with 100 ml of ethanol. The crude product was washed three times with methanol (3×500 ml) and then two times with acetone (2×350 ml) to remove unreacted monomers. Then, the compound was dried at 70 °C under vacuum for 12 h.

Results are given as follows. Yield: 87%; white solid; mp. 132 °C; ^{1}H NMR (200 MHz, $CDCl_3$, TMS) [ppm]: δ 8.41 (s, 2H, C**H**=N–); 7.88–7.93 (d, 4H, **H$_{Ar}$**), 7.62–7.66 (d, 2H, **H$_{Ar}$**-); 7.01–7.06 (d, 2H, **H$_{Ar}$**–O); 4.14–4.19 (m, 2H, C**H**$_2$–O); 2.30 (m, 2H, CH_2–C**H**$_2$–CH_2–CF_2); 1.59 (m, 2H, C**H**$_2$–CF_2). ^{13}C NMR (50 MHz, $CDCl_3$, TMS) [ppm]: δ 163.93, 155.95, 155.68, 146.84, 144.76, 142.65, 139.15, 135.40, 132.02, 130.21, 128.22, 127.24, 120.85, 115.71, 114.67, 114.65, 99.77, 66.63, 64.19, 60.96, 33.76, 32.12, 29.69, 16.73. Anal. Calcd for $C_{32}H_{15}NOF_{34}$ (1075): C, 35.72; H, 1.40; N, 1.30. Found: C, 35.80; H, 1.48; N, 1.35.

2.3.1. Device fabrication

Current–voltage measurements were performed on an ITO/Az/Al device. Samples were prepared on ITO-glass substrates, which were cleaned in an ultrasonic washer and organic solvents (isopropanol, toluene and acetone). On ITO, glass substrates compounds were spread using a spin-coating method with an angular speed of 880 turns/min by 10 s. After that, samples were annealed every 3 h at 50 °C. Then, the aluminum electrode was spread by thermal evaporation using vacuum gadgetry at 5×10^{-4} Torr. Electrical measurements were performed in the dark and during irradiation with light (under illumination of 1000 W/m^2). A halogen lamp was used as the light source.

3. Results and discussion

The methodology for the synthesis of the imine **Az** is depicted in Fig. 1. The reaction between 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy)benzaldehyde and 4-(heptadecafluorooctyl)aniline in N,N-dimethylacetamide (DMA) medium at 160 °C gave the imine **Az**. The crude product was washed three times with methanol and then two times with acetone to remove unreacted amine and aldehyde. Additionally, the compound was characterized by thin layer chromatography (TLC; developing solvent dichloroethane/ethyl acetate, 50/50). Analytical thin layer chromatography (TLC) was performed on silica gel plates from E. Merck (silica gel F_{254}). Visualization was accomplished using iodine vapor. After the purification of **Az** with methanol and acetone, the TLC analysis showed only one dot, and no substrates (amine and aldehyde) that can be easily detected or isolated were found.

The compound was characterized by ^{1}H and ^{13}C NMR spectroscopy and, additionally, by the elemental analysis. A one proton singlet at about δ = 8.41 ppm shows the formation of the imine. In the carbon NMR spectrum, the signal at δ = 161 ppm confirms the existence of the azomethine group carbon atoms. The elemental analysis shows good agreement of the calculated and found content of carbon, nitrogen and hydrogen atoms in the **Az**.

The changes in the chemical shift in NMR spectra, observed from the modification of the chemical constitution of the amine, were not observed. For the imine obtained from 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-