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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.

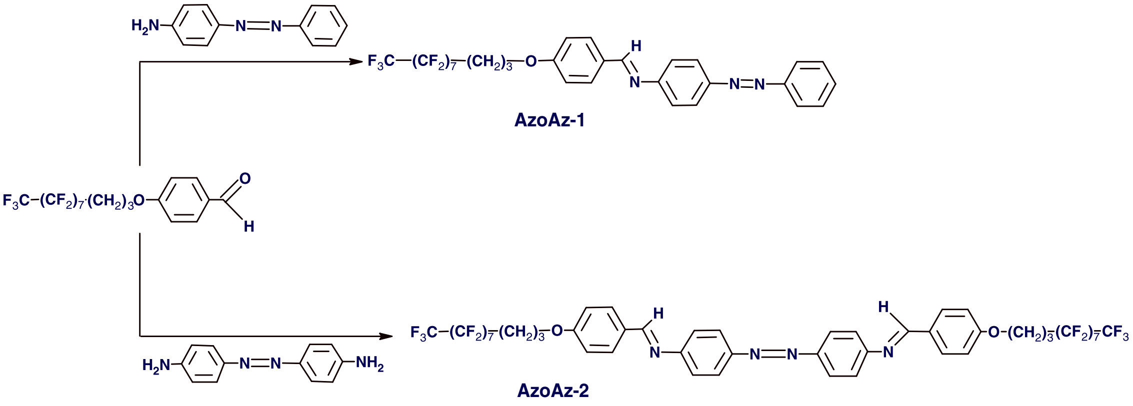

Fig. 1. Synthetic route and chemical structure of the synthesized azobenzeneimines.

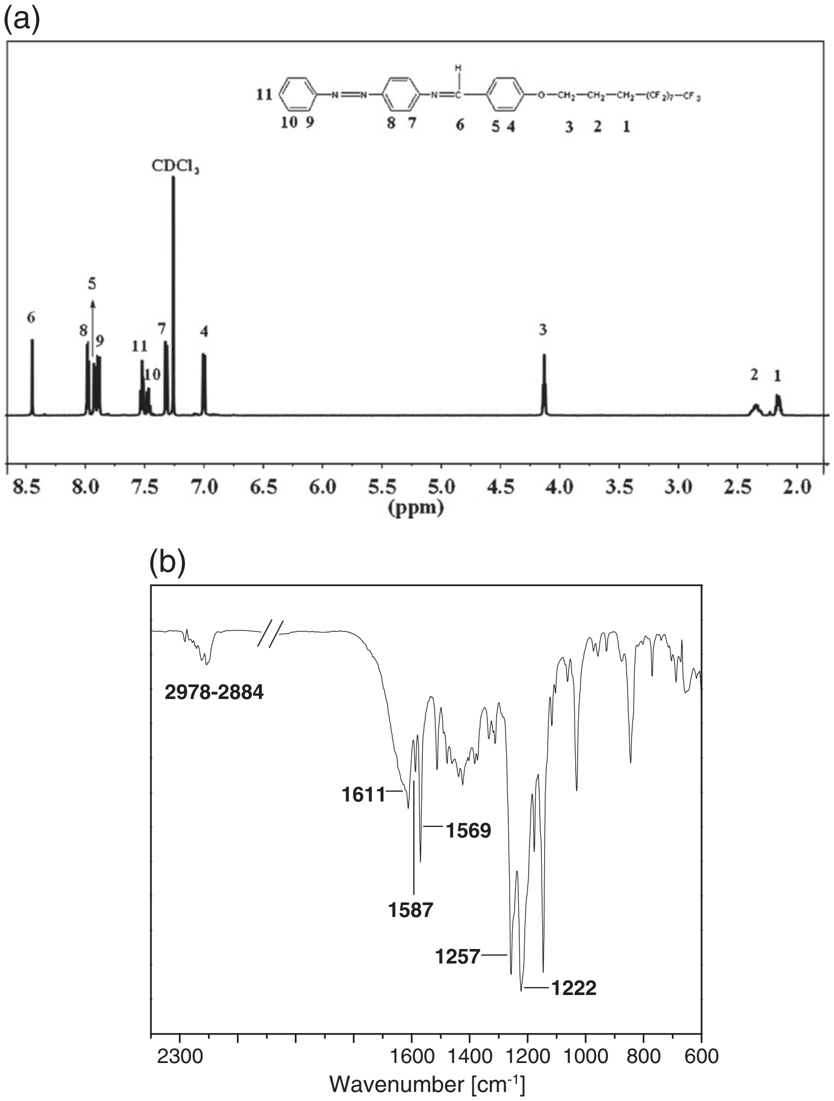

Fig. 2. ^{1}H NMR (a) and FTIR (b) spectra of AzoAz-1.

2. Experimental

2.1. Materials

4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyloxy) benzaldehyde), 4-aminoazobenzene, N,N-dimethylacetamide, p-toluenosulfonic acid (PTS), methanol were purchased from Aldrich Co. and were used without any purification. 4,4′-Diaminoazobenzene was synthesized according to published procedure [30].

2.2. Synthesis of 4, 4′-diaminoazobenzene

4-(4-Nitrophenylazo) aniline (Orange 3) (5 mmol, 1.21 g) was dissolved in 100 ml of methanol and then $Na_2S \cdot 9H_2O$ (1.2 mmol, 2.88 g) solubilized in water (120 ml) was added dropwise for 1 h. The mixture was refluxed for 3 h at 85 °C. The product was precipitated with cold water, collected by filtration and washed three times with 100 ml cold water and dried under vacuum at 100 °C.

Dark brown powder. Yield 90%. ^{1}H NMR (600 MHz, $CDCl_3$, TMS) [ppm]: δ = 7.51 (d, 4H, ArH); 6.61 (d, 4H); 5.69 (s, 4H, $-NH_2$). Mp: 244 °C. FTIR (KBr) [cm^{-1}]: 3474, 3376, 3340, 3203, 1616, 1591, 1504, 1301, 1239, 1143, 1116, 836, 752, 729, 693, 645, 547.

2.3. Synthesis of azobenzeneimines AzoAz

4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyloxy) benzaldehyde (0.5 mmol, 0.29 g) and 4-aminoazobenzene (0.5 mmol, 0.09 g) (or 4,4′-diaminoazobenzene (0.25 mmol, 0.05 g) in 5 ml of N,N-dimetylacetamide (DMA) solution with 0,06 g of PTS were added into round-bottomed flask. The mixture was refluxed with stirring for 10 h at 160 °C under argon atmosphere. The solution was cooled to room temperature and poured into methanol. The precipitated compounds were filtered, washed with methanol and dried at 70 °C under vacuum.

AzoAz-1: Orange powder. Yield 76%. ^{1}H NMR (600 MHz, $CDCl_3$, TMS) [ppm]: δ = 8.44 (s, ^{1}H, HC═N); 7.98 (d, 2H); 7.92 (d, 2H); 7.89 (d, 2H); 7.52 (t, 1H); 7.48 (t, 2H); 7.32 (d, 2H); 6.99 (d, 2H); 4.13 (t, 2H, $-OC\mathbf{H_2}-$); 2.35 (m, 2H, $-C\mathbf{H_2}-$); 2.15 (t, 2H, $-C\mathbf{H_2}-CF_2-$). FTIR (KBr) [cm^{-1}]: 2978, 2923, 2884, 1611, 1587, 1569, 1512, 1424, 1333, 1312, 1257, 1222, 1177, 1146, 1116, 1062, 1031, 957, 927, 844, 770, 687, 655, 598, 555. Anal.Calcd. $C_{30}H_{20}N_3OF_{17}$: C, 47.87%; H, 2.65%; N, 5.52%. Found: C, 47.08%; H, 2.70%; N, 5.44%. Mp: 101 °C.

Table 1
Thermal parameters of the azobenzeneimines determined by DSC.

Code	Heating rate [°C/min]	Phase transitions [°C] (corresponding enthalpy changes [J/g])	
		Heating	Cooling
AzoAz-1	2.5	57.5 (19.7), 100.6 (33.5), 121.6 (2.2), 274.5 (12.2)	46.6 (11.1), 114.7 (1.9), 229.4 (3.9), 271.6 (11.3)
	5	58.8 (13.6), 101.7 (39.8), 124 (3.2), 275.2 (11.9)	47.5 (10.1), 119.8 (3.3), 273.9 (13.2)
AzoAz-2	2.5	112.7 (13.6), 160.1 (5.9), 202. (1.8), 288 (1.7), 327.4 (5.9)	85.7 (10.7), 147.3 (4.3), 203.1 (2.9), 277.6 (5.9), 313.1 (0.4)
	5	105.4 (13.9), 152.4 (5.4), 200.1 (4.5), 326.8 (1.9)	84.3 (13.9), 146.8 (4.1), 201 (4.6), 315.7 (2.2)

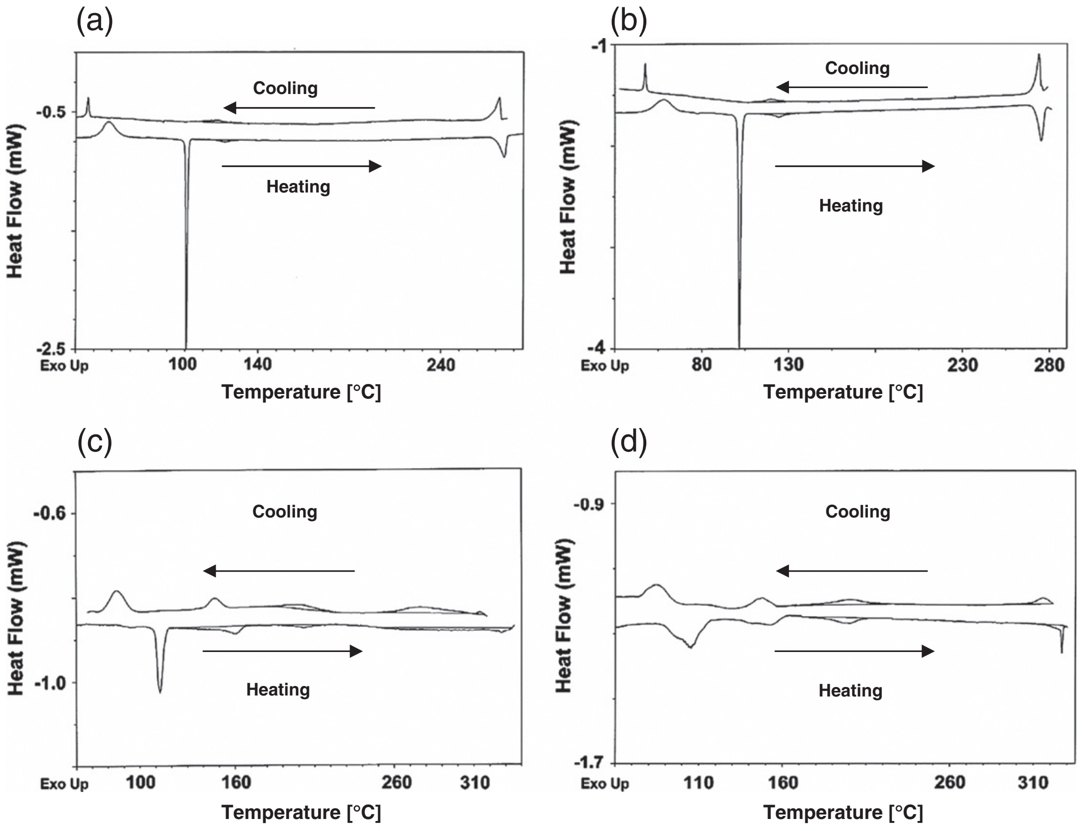

Fig. 3. DSC curves of the (a) AzoAz-1 at the heating and cooling rate 2.5 deg/min, (b) AzoAz-1 at heating and cooling rate 5 deg/min, (c) AzoAz-2 at heating and cooling rate 2.5 deg/min and (d) AzoAz-2 at heating and cooling rate 5 deg/min under N_2 atmosphere.

AzoAz-2: Light brown powder. Yield 85%. ^{1}H NMR (600 MHz, $CDCl_3$, TMS) [ppm]: $\delta = 8.44$ (s, 1H, HC=N); 7.97 (d, 4H); 7.87 (d, 4H); 7.58 (d, 4H); 6.98 (d, 4H); 4,12 (t, 4H, $-OCH_2-$); 2,33 (m, 4H, $-CH_2-$); 2,15 (t, 4H, $-CH_2-CF_2-$). FTIR (KBr) [cm^{-1}]: 2984, 2961, 2886, 1609, 1587, 1568, 1512, 1478, 1422, 1402, 1372, 1332, 1312, 1256, 1223, 1176, 1148, 1117, 1062, 1030, 972, 957, 847, 738, 704, 671, 657, 616, 560, 530, 510.Anal.Calcd. $C_{48}H_{30}N_4O_2F_{34}$: C, 42.99%; H, 2.25%; N, 4.18%. Found: C, 41.86%; H, 2.22%; N, 3.89%. Mp: 112 °C.

2.4. Measurements

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on an Avance II Ultra Shield Plus Bruker MT 600 MHz spectrometer using chloroform ($CDCl_3$) as solvent and TMS as the internal standard. FTIR spectra were measured on a 560 MAGNA-IR NICOLET Spectrometer (pellets in KBr). Elemental analyses were performed using Perkin Elmer Analyzer 2400. Differential scanning calorimetry (DSC) was performed with a TA-DSC 2010 apparatus (TA Instruments), under nitrogen atmosphere using sealed aluminum pans at heating/cooling cycles. The transition temperatures were taken as maximum of the endothermic and exothermic peaks. The textures of the liquid-crystalline phase 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 spectra were recorded using JASCO V-570 (UV–vis-NIR) spectrophotometer. Photoluminescence spectra were registered on a fluorescence spectrophotometer Hitachi F-2500 (xenon lamps as the light source). Current–voltage characteristics were detected using Keithey 6715 electrometer.

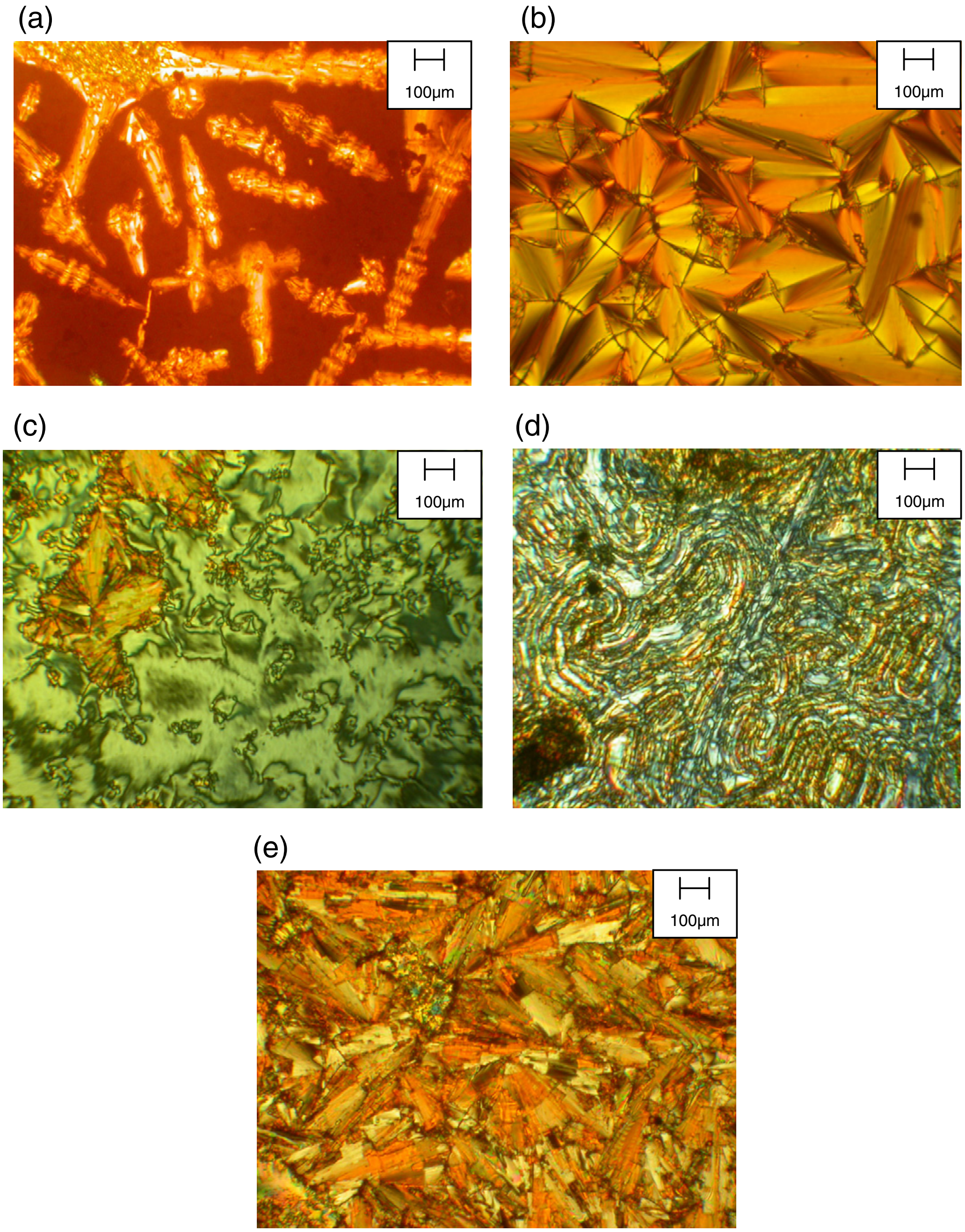

Fig. 4. Optical textures of AzoAz-1 at: (a) 270 °C, (b) at 250 °C, (c) at 112 °C, (d) at 60 °C, and (f) at 40 °C.

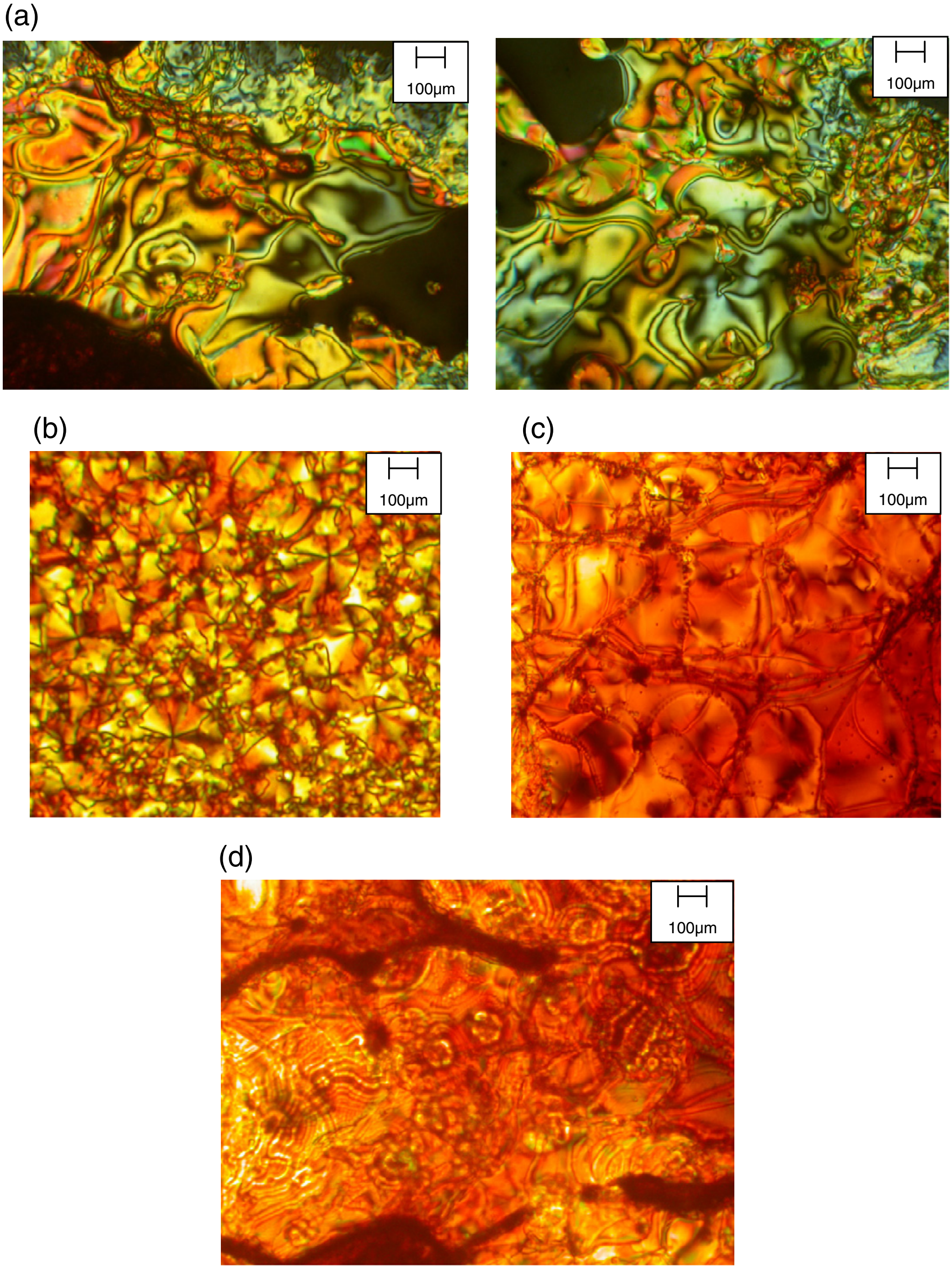

Fig. 5. Optical textures of AzoAz-2: (a) at 299 °C, (b) at 272 °C, (c) at 195 °C, and (d) at 120 °C.

3. Results and discussion

The aim of this work is development of new photochromic liquid crystalline azobenzene compounds, which could be promising for applications in optoelectronics and photonics. In the present study two new LC imines containing azobenzene unit based on heptadecafluoroundodecyloxy benzaldehyde were synthesized and characterized.

Table 2
Identified mesophases of the azobenzeneimines determined by POM.

Code	Phase transitions [°C] cooling POM
AzoAz-1	I 276 °C, SmA 271 °C, SmX 114 °C, Cr 46 °C
AzoAz-2	I 330 °C, N 313 °C, SmA, 277 °C SmX2 203 °C, SmX1 147 °C, Cr 85 °C

Cr — crystal, SmA — smectic, SmX — mesophase, N — nematic and I — isotropic phase.

3.1. Synthesis and characterization

The azomethines with azobenzene unit denoted as AzoAz-1 and AzoAz-2, were obtained in a one step condensation reaction between 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy) benzaldehyde and 4-aminoazobenzene (AzoAz-1) and 4,4′-diaminoazobenzene (AzoAz-2). Reactions were carried out in DMA solution in the presence of a catalytic amount of PTS. The reaction route and chemical structure of the obtained azoimines are given in Fig.1.

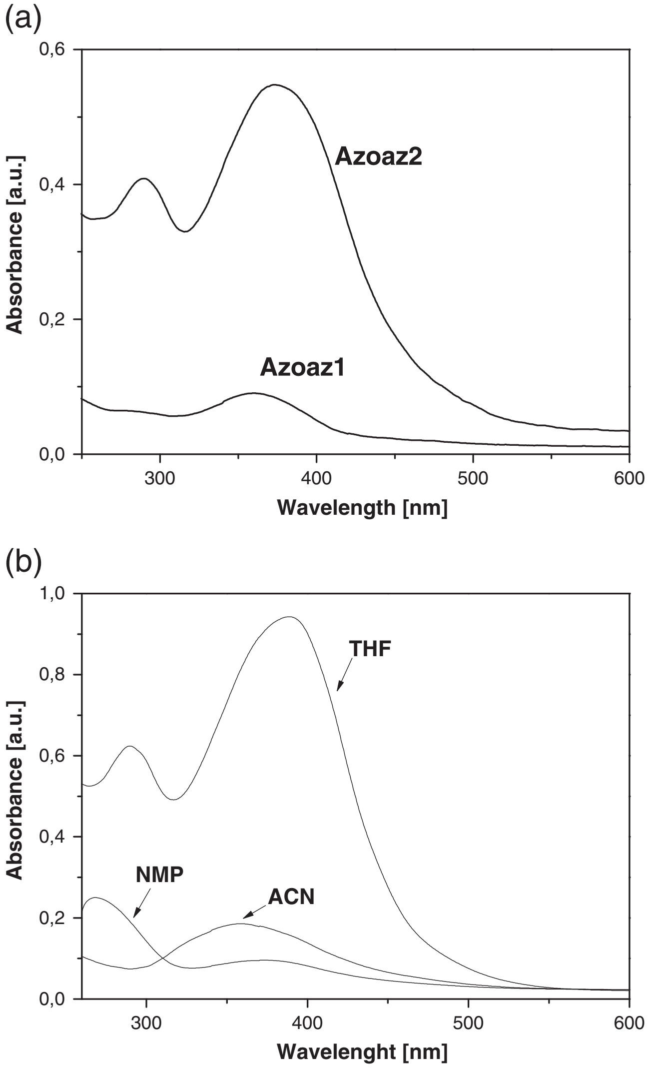

Fig. 6. UV–vis absorption spectra (a) of AzoAz-1 and AzoAz-2 in chloroform solution (b) and of AzoAz-2 in various solvent at concentration 10^{-5} mol/L. Solvents: THF-tetrahydrofuran, ACN — acetonitrile, NMP-N-methyl-2-pyrrolidone.

The condensation of heptadecafluoroundodecyloxy benzaldehyde with 4-aminoazobenzene gives unsymmetrical azobenzeneimine (AzoAz-1), while with 4,4′-diaminoazobenzene results in symmetrical azomethine (AzoAz-2). The formation of AzoAz-1 and AzoAz-2 was confirmed by ^{1}H NMR, FTIR and elemental analysis. Fig. 2 illustrates typical ^{1}H NMR and FTIR spectra of obtained AzoAz-1 which are characteristic as well as for the synthesized AzoAz-2.

The absence of the aldehyde and amino groups were confirmed by ^{1}H NMR and FTIR spectroscopies. In proton NMR spectra of the investigated compounds the azomethines proton signal was observed at 8.44 ppm (cf. Fig. 2a). The presence of imine group was also confirmed by FTIR spectroscopy since in each case the band characteristic of the ($-$HC$=$N$-$) stretching deformations was detected. The exact position of this band is almost the same for both imines, namely 1611 cm^{-1} and 1609 cm^{-1} for AzoAz-1 and AzoAz-2. In addition to the imine band, the bands at 1568 cm^{-1} and 1582 cm^{-1} can be distinguished to the ($-$C$=$C$-$) and ($-$N$=$N$-$) stretching deformations in the aromatic rings and in azo linkages [12], respectively. Moreover, in AzoAz FTIR spectra the bands at 1257 cm^{-1} and 1223 cm^{-1} were observed, which are ascribed to the stretching vibration in the ether linkages ($-$C$-$O$-$C$-$) and ($-CF_3$) units, respectively. The absorption bands characteristic for aliphatic C$-$H stretch are seen in the spectral range 2978–2884 cm^{-1}. Elemental analysis shows good agreement of the calculated and found content of carbon, nitrogen and hydrogen in the AzoAz compounds.

3.2. Liquid crystalline properties

The mesomorphic properties of the new symmetrical and unsymmetrical azobenzeneimines were determined by means of differential scanning calorimetry (DSC) and polarized optical microscopy (POM). DSC experiments were carried out under nitrogen atmosphere using two different heating and cooling rates in a temperature range from 20 °C to over the clearing point. The obtained results indicated that both compounds exhibited liquid crystalline properties. Details of the transition temperatures and associated enthalpy change of the azobenzeneimines determined by DSC are summarized in Table 1.

Differences in liquid crystalline properties of AzoAz-1 and AzoAz-2 are clearly observed. It was found that the second imide bond and alkoxyfluoritanted chain influenced on AzoAz-2 mesomeorphic properties. The symmetrical azobenzeneimine AzoAz-2 exhibited a cleaning point at temperature higher about 50 °C than the unsymmetrical azobenzeneimine AzoAz-1. DSC thermograms of the studied azoimines are shown in Fig. 3.

All the DSC thermograms for the azobenzeneimines showed multiple melting peaks, indicated the presence of mesophases. Parameters of heating and cooling process of azobenzeneimines were similar and AzoAz exhibited reversible thermal behavior. It should be noted during heating of the AzoAz-1 so called “cold” crystallization was observed at around 58 °C. Whereas symmetrical azobenzeneimine did not show “cold” crystallization. The phase transitions were analyzed in terms of their enthalpy values as well. The melting process has the highest enthalpy values (cf. Table 1). The enthalpy values under the heating trace decreased from 39.8 J/g for AzoAz-1 to the minimal value 1.9 J/g for AzoAz-2. Phase behavior of both compounds was investigated additionally by polarized optical microscopy. Photomicrographs of the optical texture of mesophases obtained for azobenzeneimines are presented in Fig.4 and Fig.5. Table 2 identifies the phase textures of investigated compounds determined by POM.

Both compounds formed stable smectic (Sm) mesophases and in the case of symmetrical azobenzeneimine nematic (N) mesophase was

Table 3
UV–vis and photoluminescence data of the azobenzeneimines in various solvents (concentration 10^{-5} mol/L).

Solvent	UV–vis				PL	
	AzoAz-1		AzoAz-2		AzoAz-1	AzoAz-2
	λ_{max} [nm]	$\varepsilon^{\#}$ [Lmol^{-1} cm^{-1}]	λ_{max} [nm]	$\varepsilon^{\#}$ [Lmol^{-1} cm^{-1}]	λ_{em} [nm]	
Acetone ($\varepsilon^{*}=2.7$)	357	16,451	359	16,345	404	518; 557
Acetonitrile ($\varepsilon^{*}=37.5$)	250; 275; 357;	11,162; 8442; 9824	223; 358	166,796; 18,569	427	500
NMP ($\varepsilon^{*}=32.2$)	261; 365	34,800; 7000	268; 370	25,032; 9588	433	507
Chloroform ($\varepsilon^{*}=4.8$)	281; 360	6400; 9055	290; 373	40,976; 54,765	439	520
THF ($\varepsilon^{*}=7.6$)	296; 362	32,100; 10,700	289; 389	62,397; 94,291	407	518

ε^{*} — dielectric constant; $\varepsilon^{\#}$ — molar absorption coefficients.

observed as well. Preliminary POM observations, on cooling from the isotropic state, showed that the compound AzoAz-1 exhibited a battonet texture typical for the smetic A (SmA) mesophase [cf. Fig. 4a] at 277 °C and focal conic texture at 250 °C [cf. Fig. 4b]. On further cooling the unsymmetrical imine showed the Schlieren (probably SmC) texture at temperature below 112 °C and a highly ordered Sm mesophase below 61 °C [cf. Fig. 4c–e]. Photomicrographs of the optical texture of AzoAz-2 mesophases revealed a nematic texture (Schlieren) at 299 °C (cf. Fig. 5a), a focal conic texture at 272 °C [cf. Fig. 5b] and two higher ordered Sm phases (cf. Fig. 5c and Fig. 5d). It can be seen that DSC/POM analysis showed that the investigated compounds exhibited complex mesomorphic transitions. In the case of unsymmetrical AzoAz-1 three transitions, namely crystal-to-mesophase (Cr/SmX), mesophase-to-smetic A (SmX/SmA), smectic A-to-isotropic (SmA/I) were detected. On other hand, the symmetrical AzoAz-2 exhibited richer polymorphism, that is, five transitions, crystal-to-mesophases (Cr/SmX1), mesophase-to- (SmX1/SmX2), mesophase-to-smectic A (SmX2/SmA), smectic A-to-nematic (SmA/N) and nematic-to-isotropic (N/I) were found. Identification of mesophases and the sequence of phase transitions were based on information provided by two references concern liquid crystals [31,32] and confirmed by repeat POM and DSC experiments.

It is interesting to compare our results with published data. To the best of our knowledge, the liquid crystalline compounds containing their structure both imine linkage and azobenzene unit were reported in four articles [20–23]. Imire et al. reported tetramers consist of four mesogenic units, namely containing azo and imine linkages, linked via a flexible spacer [22]. The influence of number of methylene units in the outer spacer on transition temperatures was investigated. These compounds exhibited two phase transitions, that is, crystal-to-nematic and nematic-isotrop in the temperature range of 197–240 °C and 213–291 °C, respectively. Rezvani et al. described LC properties a series of azo-linked salicylidenic Schiff bases [22]. It was found that the obtained compounds with long alkyl length exhibited thermodynamically stable enantiotropic mesophase (SmA) but with short length showed monotropic unstable phase with isotropisation temperature from 119 to 122 °C. Iwan et al. reported LC azoazomethines obtained from 4-((4-aminophenyl)diazenyl)-N,N- dimethylbenzamine and 4-biphenyl carboxyaldehyde denoted as **4** and from the same aldehyde which we used in the our work, namely 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy)benzaldehyde denoted as **F4** [20,22]. Azoimine **F4** structurally similar to AzoAz-1, exhibited higher temperature of phase transitions (DSC, heating run), that is, 118.7 °C, 202.2 °C and 294.4 °C and no "cold" crystallization was detected compare to AzoAz-1. Based on POM experiment the azomethine **F4** had two enantiotropic mesophases such as SmX (240 °C) and SmA (290 °C) similar to AzoAz-1 which showed also SmX (115 °C) and SmA (272 °C) mesophases. Totally different kinds of mesophases and phase transition temperatures were found for imine **4** described by Ivan et al. and Henderson et al. [20,22].

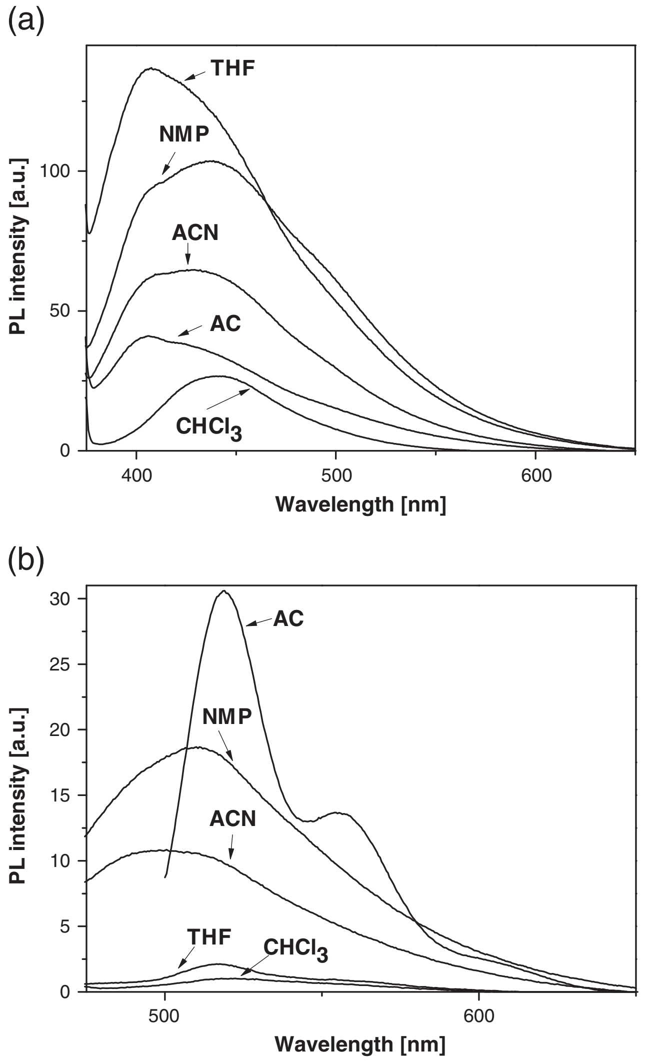

Fig. 7. PL emission spectra in various solvent of (a) AzoAz-1 under excitation 359 nm and (b) AzoAz-2 under excitation 450 nm. Solvents; THF-tetrahydrofuran, NMP-N-methyl-2-pyrrolidone, ACN — acetonitrile, AC — acetone.

Additionally, the influence of various heating and cooling cycles rates on LC properties of azobenzeneimines were investigated by DSC. It was found that decreasing the heating rate from 5 to 2.5 deg/min caused small changes in DSC traces of AzoAz-1 (cf. Table 1, Fig. 3). In the case of symmetrical azobenzeneimine AzoAz-2 during heating rate 2.5 deg/min five phase transitions were observed while under faster heating rate (5 deg/min) four transitions were found. Probably the kinetic of mesophase transition detected at 288 °C under heating rate 2.5 deg/min was too slow to be seen at heating 5 deg/min and this mesophase needs more time to structured.

3.3. Optical properties

The optical properties of the new azobenzeneimines were analyzed by UV–vis absorption and photoluminescence (PL) spectroscopies. UV–vis and PL spectra of azobenzeneimines were acquired in various solvents at a concentration 10^{-5} mol/L. The range of the measurements was limited by the transparency of used solvent. The absorption spectra of the AzoAz in chloroform solution are illustrated in Fig.6a.

Electronic absorption spectra of studied azobenzeneimines showed similar characteristics, that is, absorption band with the maximum (λ_{max}) located in the range of 360–373 nm, which is attributed to the electronic transition of the *trans*-azochromophore ($n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$) [33]. This band is clearly separated from the absorption in the UV region in the range of 281–290 nm, which can be ascribed to the imine bond [34]. The introduction of second both azomethine linkage and alkoxyfluoronated chain in to azobenzeneimine compound (AzoAz-2) resulted in bathochromic shift of a λ_{max} position compare to AzoAz-1. Moreover, the band at higher energy region is much better structured in the case of the symmetrical azobenzeneimine (AzoAz-2). Absorption spectral data of studied compounds are summarized in Table.3.

The values of molar extinction coefficients (ε_{max}) calculated at λ_{max} of azobenzene absorption band were higher for symmetrical azobenzeneimine (AzoAz-2) compare to AzoAz-1 (except for spectrum recorded in acetone). The high-value of the absorption coefficients suggests the high probability of electron transition and the enhancement of absorption efficiency [35].

Additionally, the solvatochromism of the compounds was evaluated. This was carried out in solvents with a different dipole moment and consequently with a different polarity, namely acetonitrile, NMP, THF,

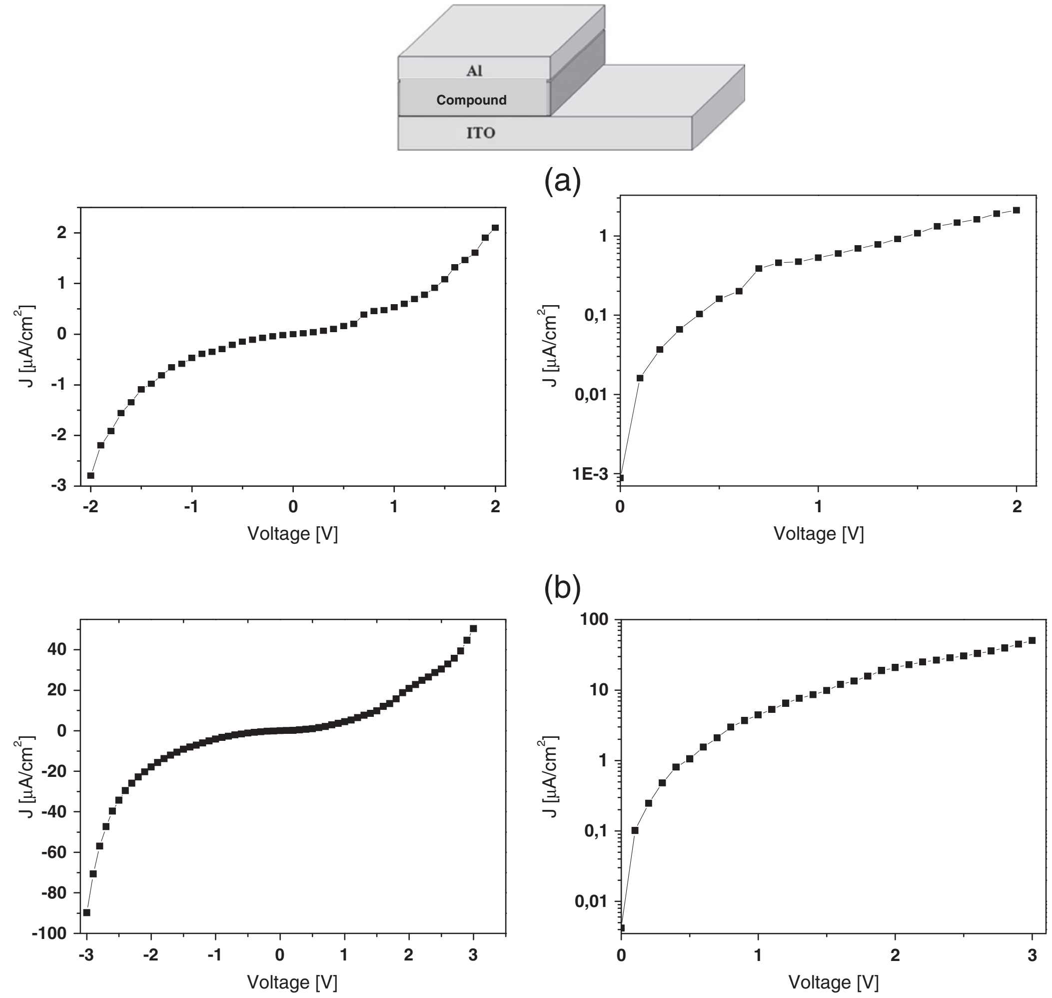

Fig. 8. Current density–voltage curves of devices: (a) ITO/AzoAz-1/Al and (b) ITO/AzoAz-2/Al and scheme of the device investigated in this work.

chloroform and acetone. Fig. 6b parents exemplary UV–vis spectra of AzoAz-2 in different solvents. It was observed that the absorption spectra of the compounds showed a strong dependency on the solvent. Considering molar extinction coefficients, the highest ε_{max} value of azobenzene transition was found in THF for AzoAz-2 and in acetone for AzoAz-1. Moreover, the ratio a ε_{max} value of bands characteristic for azobenzene unit and azomethine bond was changed in relation to kind of solvent (cf. Table 3 and Fig.6b). In the case of absorption spectra of AzoAz-2 recorded in NMP and acetonitrile solution band ascribed to imine linkage was much intense. On the other hand, AzoAz-1 exhibited lower ε_{max} value of azobenzene band in THF and NMP solution. In the case of AzoAz-1 despite the different polarity of the applied solvents, the spectra showed a λ_{max} position at almost the same wavelength (cf. Table 3) therefore; the solvatochromic effect was not observed. The imine AzoAz-2 exhibited the same a λ_{max} position of azobenzene absorption band in the solvents with the highest differences in polarity, namely acetone ($\varepsilon = 2.7$) and acetonitrile ($\varepsilon = 37.5$). However, the bathochromic shift (about 30 nm) of λ_{max} was detected in absorption spectrum of symmetrical azobenzeneimine in THF solution in relation to acetonitrile and acetone. Taking into consideration UV–vis spectra of AzoAz-2 recorded in acetone, chloroform and THF solution the negative solvatochromism was observed. In these solvents with increasing polarity is hypsochromic shift towards blue light [cf. Table 3]. The negative solvatochromism indicates that with increasing solvent polarity, the ground-state molecules of the compounds are better stabilized by solvatation than the molecules in the exited state [35].

Photoluminescence (PL) properties of azoimines were investigated at concentration of 10^{-5} mol/L in such solvents as acetone, acetonitrile, NMP, chloroform and THF. Fig. 7 presents emission spectra of azobenzeneimines in various solvents while the emission spectral data are summarized in Table.3.

In most cases both azobenzeneimines exhibited a single broad emission band (except for AzoAz-2 in acetone) with the maximum (λ_{em}) located in the violet-blue region and also in the green range.

In the case of AzoAz-1, the emission spectra showed that λ_{em} hypsochromically shifted compared to AzoAz-2. Considering fluorescence emission intensity it was found that higher intensity exhibited unsymmetrical azobenzeneimine AzoAz-1 than AzoAz-2 (cf. Fig. 7). The influence of solvent on PL properties was found. The highest emission intensity of AzoAz-1 was observed in THF solution while in the case of AzoAz-2 the highest emission intensity in acetone was detected [cf. Fig. 7a]. Both compounds exhibited the lowest emission intensity in chloroform solution. Taking into account the influence of solvent polarity on λ_{em} position it is difficult to find clearly seen relationships.

3.4. Current–voltage measurement

The materials with imine units are investigated as hole transporting compounds. In order to investigate the usefulness of synthesized new imines as hole-transport materials a preliminary study of current–voltage characteristic were performed. Devices with the following architecture: ITO/compound/Al were constructed and investigated at room temperature. Indium-tin oxide (ITO)-coated glass was applied as the bottom electrode and was coated with AzoAzs an active layer. Aluminum was thermally deposited in vacuum (~10^{-6} Torr) as a top electrode. In all these devices the ITO electrode was used as the anode, whereas the top metallic contact was the cathode. The Al forms the Schottky barrier with azomethine while ITO forms the ohmic contacts. The electrical behavior of devices in ambient conditions under both forward and reverse bias was studied. Forward bias is defined here as a positive bias on the bottom ITO electrode, i.e. a positive bias on the p-type organic layer relative to the top contact which is expected to be the main rectifying barrier [36]. The electrical behavior of devices measured under forward and negative bias follows a characteristic pattern shown in Fig. 8.

The current density–voltage (J–V) traces have shapes similar to sigmoidal, which has a linear section inside. The shape of J–V characteristics confirms semiconducting nature of investigated compounds. The turn-on voltage of the devices was observed below 1 V. However, at this step of the project it is impossible to compare the conductivity of the samples, because the knowledge of their geometry (thickness and surface) is necessary. The devices showed very little rectifying behavior with lager currents than in forward bias similar [36]. Relatively not so high current densities were observed. Higher J value exhibited device with symmetrical azobenzeneimine AzoAz-2 as organic layer. However, the increase of device performance can be obtain by modification of its architecture, that is, by adding interfacial layer of poly(3,4-ethylenedioxythiphene (PEDOT) or PEDOT doped with polystyrene sulfonic acid (PSS), by utilization of another cathode or mixing AzoAz with an n-type compound [37,38]. Further investigations are in progress.

4. Conclusion

In summary, two new liquid crystalline azobenzene chromophores were prepared by the 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 and 4,4′-diaminoazobenzene.

The following conclusions can be drawn from the present work.

1. Two new symmetrical and unsymmetrical azomethines containing azobenzene unit were synthesized and characterized. The molecular structures were identified by FTIR, ^{1}H NMR spectroscopy and elemental analysis, and the results were in accordance with the expected molecular formulae.
2. The obtained compounds were liquid crystalline. The introduction of second fluorinated chain and imine bond into the compound increased the transition temperature at about 50 °C but induced more reach polymorphism. Unsymmetrical azobenzeneimine showed two mesophases designated to be SmX and SmA phases while symmetrical compound exhibited four mesophases designated to be SmX1, SmX2, SmA and N.
3. The absorption band attributed to the electronic transition moment of the *trans*-azochromophore was located in the range of 360–373 nm.
4. The investigated azobenzeneimines showed fluorescence activity and the differences in emitted light wavelength were observed. The light in the green region was emitted by the symmetrical azomethine while in violet-blue range by unsymmetrical imine.
5. Preliminary study of the current–voltage characteristic for a device ITO/compound/Al confirmed their semiconducting properties.

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