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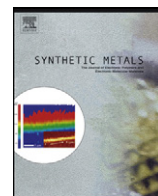


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Synthesis and study on the light absorbing, emitting, redox and electrochromic properties of azines and polyazines with thiophene units

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ABSTRACT

Low molecular weight compounds and polymers consisting of 1 and 2 thiophenes and double azomethine bonds prepared from hydrazine and thiophene aldehydes are presented. The effect of the number of thiophene rings on thermal, optical and electrochemical properties was examined. Polyazine with bithiophene structure exhibited slightly higher both glass transition temperature ($T_g = 121^\circ\text{C}$) and the decomposition temperature ($T_{10} = 345^\circ\text{C}$) than polymer with one thiophene ring in repeating unit ($T_g = 115^\circ\text{C}$, $T_{10} = 321^\circ\text{C}$). A higher degree of conjugation due to presence of bithiophene structure was confirmed by bathochromic shift of the absorbance and photoluminescence. Doping with HCl and FeCl_3 resulted in increase of fluorescence intensity. All the obtained compounds emitted blue light with the highest intensity both in solution and in solid state as a blend with PMMA. The investigated compounds exhibited electrochemical energy gap (E_g) in the range of 1.94–3.07 eV. Introduction of a second thiophene ring resulted in a decrease of E_g by about 0.9 eV in the case of azines and 0.67 eV in polyazines. Additionally, energy band gap (E_g) was calculated theoretically at B3LYP/6-31G(d,p) level of theory.

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1. Introduction

Polyazines belong to an important group of polymers with conjugated chains. They are analogues of vinylene derivatives that have $\text{HC}=\text{N}$ linkages in their structure. Due to the presence of the nitrogen atom, these compounds are air-stable, in contrast to isoelectric polyacetylene [1]. Polyazines may exhibit interesting properties, such as semi-conductivity, non-linear optical response, thermal and environmental stability and also mechanical resistance [1b,2]. They are very promising materials for electronic, optoelectronic and photonic applications [1a,c,3]. The simplest polyazine, $[-\text{N}=\text{CH}-\text{CH}=\text{N}-]_n$, was obtained and characterized by Cao and Li [4]. This polymer and its methylated derivatives have been further studied by Euler and co-workers [1a,c,3a]. Their calculations indicated that the electric structure of polyazine had narrower valence and conduction band and a larger band gap than polyacetylene. However, the conducting state could be obtained by oxidative doping with iodine. The linear defect-free permethylated derivative exhibited moderate conductance [1a] and in the case

of the defect-containing unsubstituted polyazine the conductance was even lower [3a]. The studies showed that the charge carriers were bipolarons, unlike soliton-like midgaps present in polyacetylene. However, some authors suggested different conduction mechanism, connected with the forming of $\text{C}=\text{C}$ bonds instead of nitrogen ions in iodine-doped polyazine [5]. Methyl substituted oligoazines with pyridine end-capped groups, which extended the conjugation length of the oligomer, were also characterized [6].

Aromatic azines and polyazines have been widely studied because of the high values of third-order non-linear susceptibility, which are expected for these structures [1b]. Lewis, Barnes and Glaser characterized the crystallographic properties of symmetric and unsymmetric azines containing two arene rings [7]. The synthesized compounds showed nearly perfect dipole parallel alignment in the crystal structure, which is necessary to exhibit non-linear optical properties. Hydrazone dendrimers with aromatic rings have been described as materials with excellent hole-transporting properties [8]. Aromatic azine-based oligomers and polymers which may be suitable for optoelectronics have been also studied [2,3c,d]. Mukherjee et al. [2] synthesized polyazines with oligo(*p*-phenylene vinylene) units. The polymers exhibited good solubility and processability, and one of the compounds underwent *n*-doping. Azine oligomers with 1,3-indandiylidene units and 9-fluorenylidene moieties have been studied by Bethell and co-workers [3c]. These oligomers were not promising as organic conductors and were proposed as materials for

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light-emitting diodes instead, but their electroluminescence properties have not been examined. Azine-based copolymers containing 1-phenyl-1,2,3,4-tetrahydroquinoline moieties have been described as good hole transporting materials for optoelectronics, because of their high charge drift mobility, suitable ionization potentials and reduced tendency to crystallize [3d]. Azines with *N*-heterocyclic rings have been also prepared and the obtained polarized materials showed non-linear optical behaviour [9].

Different azines, polyazines and polyazomethines containing thiophene [1b,3b,10], cyclopentadithiophene [11] or 1,3-dithiole [12] moieties are described in the literature. Polyazines with 3-dodecylthiophene unit have been proposed for channel waveguides by Amari and co-workers [10a]. However, the intrinsic linear losses were too high for non-linear optical applications. Such mono-substituted polyazines were compared with didodecyl polymers and the latter exhibited enhanced overall conjugation length [10b]. The authors have also prepared other polyazines with 3-alkylthiophene and non-substituted thiophene rings [1b]. The compounds were thermally stable and showed promising electronic properties, moreover the butyl derivative had good solubility. Tindale et al. [3b] have characterized the properties of polymer obtained by electropolymerization of 1,4-dimethyl-1,4-bis(2,2'-bithien-5-yl)-azine, which is a compound similar to one of the polyazines described in our paper. The polymer exhibited cathodic photocurrents when illuminated in solution at negative potentials and its photoefficiency was 25% higher than the efficiency of non-modified polybithiophene. A series of azines with liquid crystalline properties, including compounds with thiophene rings, have been also prepared [10c]. These azines have potential use in light-emitting devices as well as in liquid crystal displays. Skene et al. [10d,e] has studied thiophene containing azomethines, which have tuneable electronic properties and exhibit multiple colour states of the oxidized forms. A series of photoconducting monomers and polymers with hydrazone moieties has been described by Getautis and co-workers [13]. These compounds had good hole drift mobility and film-forming properties and may find use as materials for electrographic photoreceptors and other optoelectronic devices.

In this paper two low molecular weight model compounds containing thiophene ring in the structure and the corresponding

polyazines are presented and their thermal (DSC, TGA), optical (UV–vis, PL), electrochemical (CV, DPV) and electrochromic properties are described. Additionally, the band gap of obtained compounds was estimated theoretically by density functional theory (DFT).

2. Results and discussion

In this article we continue our efforts in the synthesis of potential materials for optoelectronics and the new conjugated low molecular weight compounds and polymers bearing in their structure both N–N and N=C linkages and thiophene rings are presented.

2.1. Synthesis and characterization

The azines and polyazines (hereafter abbreviated as AZ and *poly*(AZ)) were prepared by condensation reaction of hydrazine and aldehydes containing thiophene or bithiophene rings. The chemical structures of the compounds synthesized in this study are presented in Fig. 1.

All compounds have been already reported in the literature [1b,14] except for polyazine obtained from 2,2'-bithiophene-5,5'-dicarboxaldehyde (*poly*(AZ2)). However, their luminescence and electrochemical and electrochromic properties have not been investigated so far. Instrumental techniques including FTIR, NMR spectroscopies and elemental analysis were applied for the characterization of the molecular structure of these compounds. The spectral data of all the compounds were found to be consistent with their molecular structures.

FTIR spectra of the azines evidence vanishing of the C=O stretching band at 1684 and 1667 cm⁻¹ with respect to the starting aldehydes. In the case of polyazines FTIR spectra indicate that this band is strongly reduced and it confirms the presence of terminal formyl groups in polymers. The appearance of the corresponding C=N stretching vibration in the spectral range 1602–1610 cm⁻¹ was detected. The exact position of this band in azines was almost the same (1608 and 1610 cm⁻¹ for AZ1 and AZ2, respectively) being shifted towards lower wavenumbers in comparison with polyazines (1604 cm⁻¹ for *poly*(AZ1) and 1602 cm⁻¹ for *poly*(AZ2)). This seems to confirm better conjugation along the

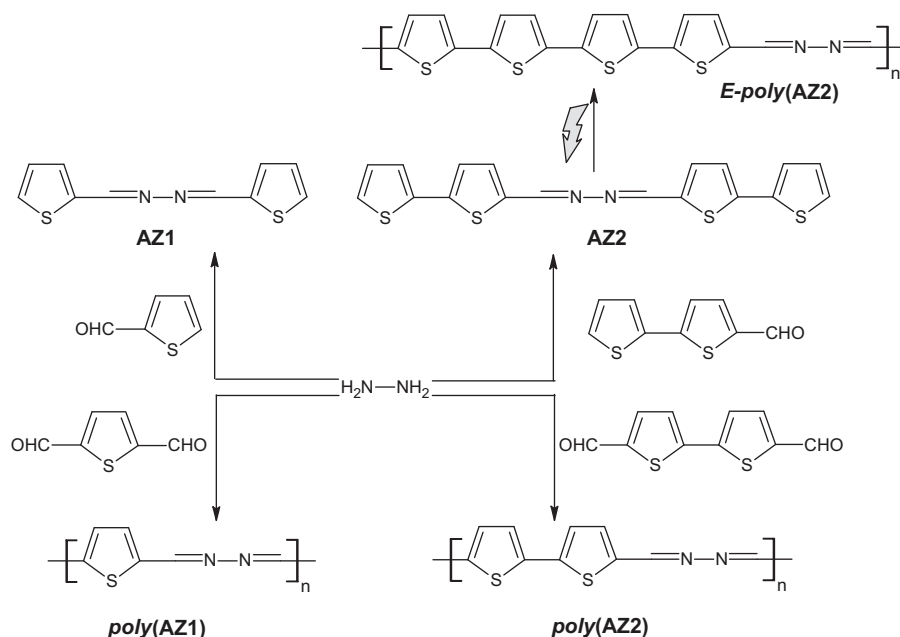


Fig. 1. Synthetic route and chemical structure of synthesized compounds.

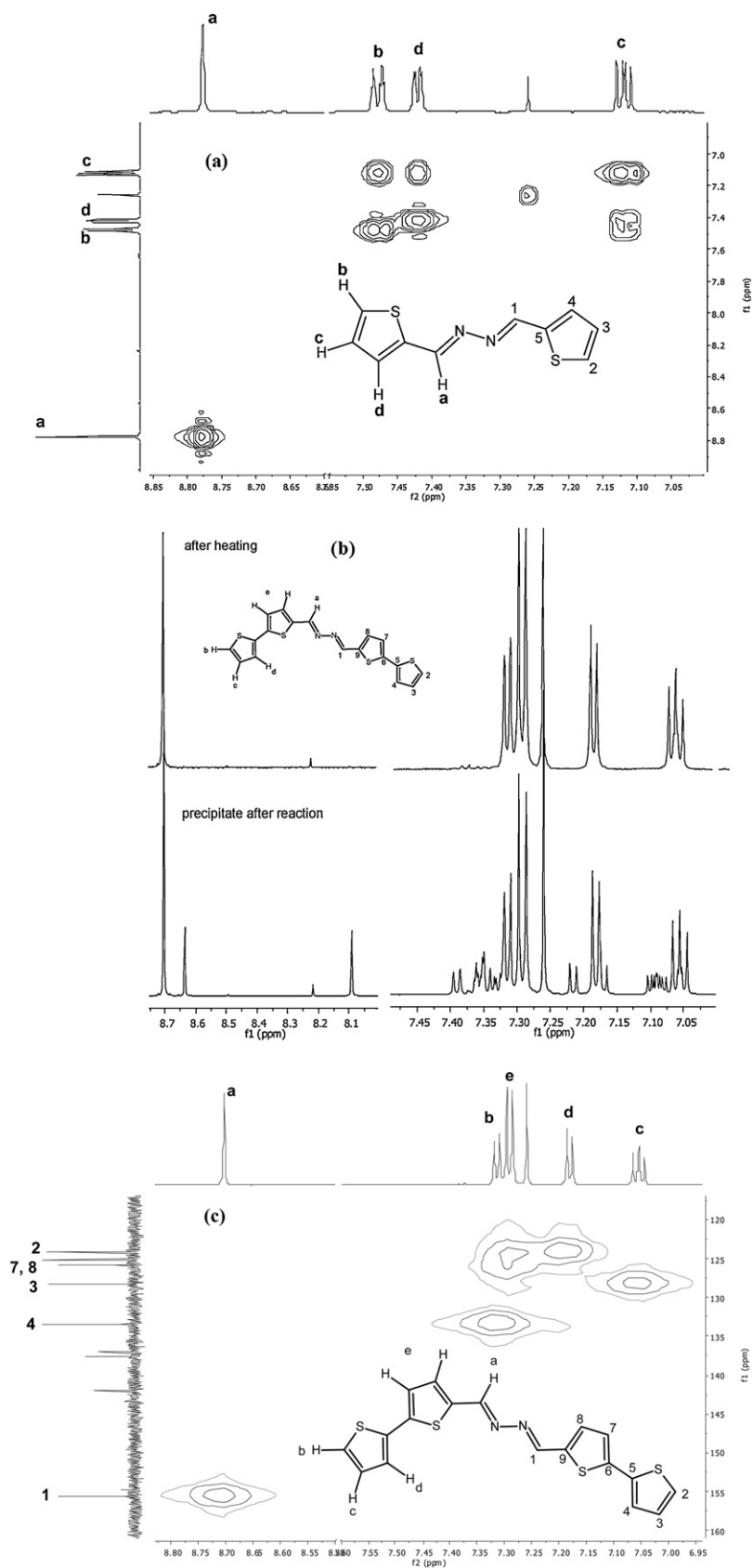


Fig. 2. NMR spectra of azines: (a) ^1H - ^1H COSY spectrum of AZ1, (b) ^1H NMR spectra of AZ2 before and after annealing and (c) ^1H - ^{13}C COSY spectrum of *E,E* isomer of AZ2.

polymer backbone in relation to low molecular weight compounds. Moreover, all compounds exhibited absorption bands in the range of 1420–1453 cm^{-1} and 1040–1062 cm^{-1} due to thiophene ring stretching ($\text{C}=\text{C}$) [10b] and azines $\text{N}=\text{N}$ stretching [3a], respectively.

The structure of model compounds was assigned on the basis of ^1H and ^{13}C NMR spectroscopy as well. In the case of polymers NMR characterization was not carried out because of its insufficient solubility. A full assignment of the resonances of the protons and carbons was achieved in two-dimensional COSY experiments. Fig. 2a presents the H–H COSY spectrum of AZ1 consisting of one singlet at 8.76 ppm which confirms the presence of $-\text{CH}=\text{N}-$ groups in the obtained compound.

Moreover, the correlated triples of doublet of doublets and doublet of triplets at 7.48, 7.42, 7.12 ppm can be easily assigned to the protons c/b/d on the thiophene ring. In ^{13}C NMR spectrum of AZ1 signal at 155.91 ppm confirms the presence of $-\text{CH}=\text{N}-$ groups along with the signals in the range of 139.15–127.96 ppm due to the presence of thiophene carbons. In the case of AZ2, in ^1H NMR spectrum of the sample obtained after synthesis, three signals at 8.70, 8.64 and 8.09 ppm (their area ratio was 10:2.5:2.5) derived from azine group were observed (cf. Fig. 2b). It suggests the formation of two isomers, with *E,E* and *E,Z* double bond configuration. The existence of two forms also was confirmed by DSC analysis. DSC thermogram of AZ2 during heating exhibited two melting endotherms at 166 °C and at 204 °C, which seems to indicate that this compound can exist in two different structures (cf. Fig. 3a). The existence of impurities was excluded considering elemental analysis results. When the sample of AZ2 was annealed in solid state at about 170 °C, in its ^1H NMR spectrum the signal at 8.70 ppm was present and signals at 8.64 and 8.09 ppm disappeared (cf. Fig. 2b). This observation contributes to the switch from *E,Z* to *E,E* isomer. In the *E,Z* isomer chemical shifts corresponding to bithiophene rings and $-\text{CH}=\text{N}-$ groups are doubled due to the broken symmetry of the molecule. In the *E,E* isomer the symmetry is regained and therefore the number of signals is reduced. Moreover, similar values of coupling constants for protons in the bithiophene moiety were observed, this may be due to enhanced conjugation in the AZ2. The similar relationship was observed in ^{13}C NMR spectra. For sample AZ2 after synthesis, signals at 155.54, 153.90 and 151.11 ppm confirm presence of two isomers, with *E,E* and *E,Z* double bond configuration. Moreover, because of too small concentration of isomer *E,Z*, signals from quaternary carbon atom were not observed. After heating signals at 153.90 and 151.11 ppm from *E,Z* isomer disappeared. Signal at 155.39 ppm confirms the presence of $-\text{CH}=\text{N}-$ groups in the AZ2 (*E,E* isomer) along with the signals in the range of 141.98–124.24 ppm due to the presence of 2,2'-bithiophene carbons. A full assignment of the resonances of the protons and carbons of *E,E* isomer of AZ2 was achieved in two-dimensional COSY experiments (cf. Fig. 2c). C–H COSY spectrum confirms that the doublet at 7.29 ppm is derived from the two protons connected to carbon atoms 7 and 8 (125.76, 124.99 ppm). The other aromatic carbons signals are well-connected with corresponding protons, as shown in the C–H COSY spectrum of *E,E* isomer of AZ2 in Fig. 2c. DFT energy calculations of compound AZ2 (with respect to the isomer used) revealed that *Z,Z* isomer is about 16 kJ mol^{-1} less stable than *E,E* isomer. However, it was also found that the isomer with mixed configuration, that is *E,Z* is about 1 kJ mol^{-1} more stable than the *E,E* one. This astonishing result may be attributed to calculation error (e.g. the basis set used, etc.) on one hand, and on the other hand this small energy difference may lead to the formation of two isomers during the reaction.

Additionally, the chemical structure of the obtained compounds was confirmed by elemental analysis. The results showed very good agreement of found and calculated content of carbon, hydrogen and nitrogen atoms for the model compounds. However, in the case of polymers the expected values of the percentages of C, H and N did

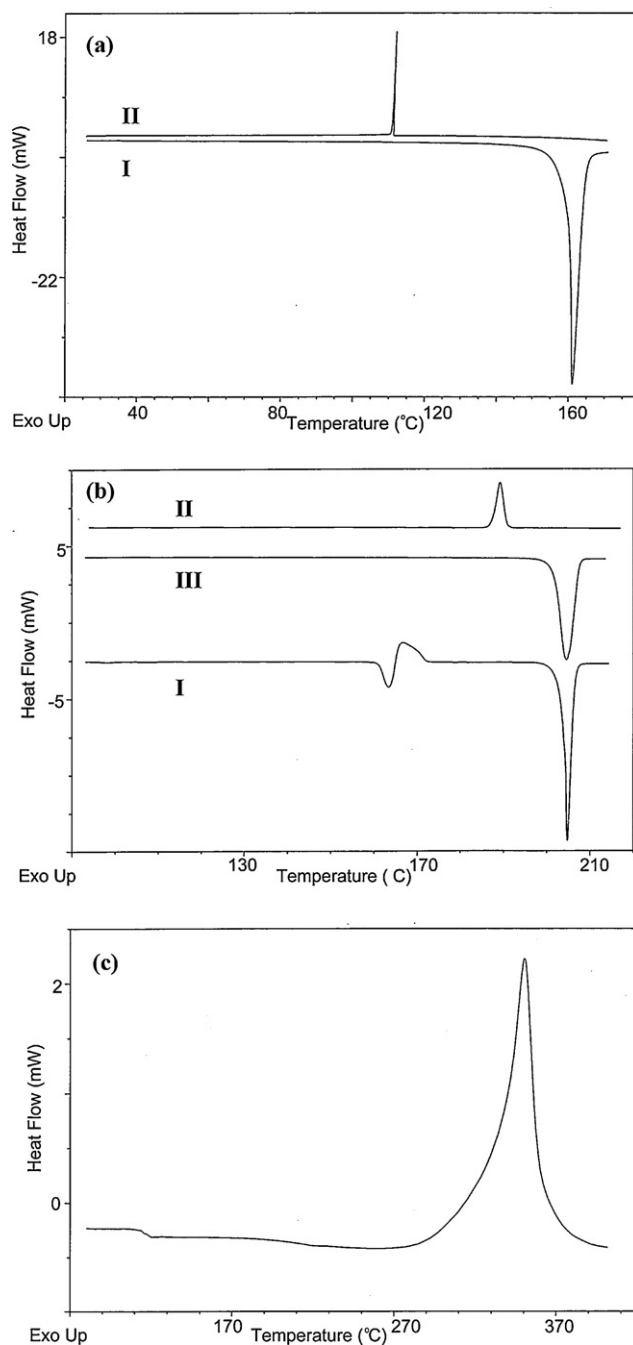


Fig. 3. DSC thermograms of (a) AZ1 where (I) heating run (2 °C/min), (II) cooling run (5 °C/min), (b) AZ2 where (I) first heating run (10 °C/min), (II) cooling run (2.5 °C/min) and (III) second heating run (10 °C/min) and (c) poly(AZ1) heating run (20 °C/min).

not agree much with the results obtained. The observed deviation in the experimental values can be explained by one or all of the following facts: (i) influence of the end group of the polymeric chain, (ii) degree of polydispersity due to polycondensation reaction and (iii) as a result of the difficulties in burning of these polymers [15].

The solubility of synthesized compounds was qualitatively determined by the dissolution of 2.5 mg of the solid in 1 mL of organic solvent at room temperature and under heating. Table 1 gives the solubility of the azines and polyazines in different organic solvents.

Taking into account the data presented in Table 1, studied AZ were soluble at room temperature in cyclohexanone and aprotic

Table 1
Solubility behaviour of the obtained azines and polyazines.

Code	Solvent CHCl ₃	NMP	DMSO	DMF	Cyclohexanone
AZ1	++	++	+	++	++
AZ2	++	++	+	++	++
poly(AZ1)	±	±	±	±	±
poly(AZ2)	±	±	±	±	±

The qualitative solubility was tested by dissolving 2.5 mg samples in 1 mL of solvent; ++ soluble at room temperature, + soluble after heating, ± partially soluble after heating. Solvents: NMP, N-methyl-2-pyrrolidone; DMSO, dimethylsulfoxide; DMF, dimethylformamide.

polar solvents such as NMP and DMF, while polyazines exhibited much lower solubility and were only partially soluble also after heating.

2.2. Thermal properties

Thermal properties of the obtained azines and polyazines were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in nitrogen atmosphere. It is clear that thermal properties of the compounds depended strongly on their chemical structure and different behaviour of AZs and poly(AZ)s was observed. Fig. 3 presents DSC thermograms of obtained azines.

DSC thermogram of the model compound AZ1 during first heating run showed one endotherm at 161 °C indicating melting of the sample (cf. Fig. 3a). During cooling exothermic peak at 113 °C confirmed crystallization of the azine. The second heating scan revealed the melting point at 163 °C. In the case of AZ2, DSC thermogram during first heating run exhibited melting endotherm at 163 °C then exothermic transition occurred with the maximum at about 166 °C followed by melting at 204 °C (cf. curve I in Fig. 3b). During cooling run exothermic peak at 189 °C was observed (cf. curve II in Fig. 3b). During second heating run the only one endotherm at 204 °C confirmed melting of the sample (cf. curve III in Fig. 3b). However, when the sample after melting was rapidly cooled in liquid nitrogen during the next heating run melting endotherm at 160 °C was detected, then exothermic transition occurred at about 163 °C being followed by melting at 203 °C. Such behaviour indicates that the model compound AZ2 after synthesis and also after rapid cooling of the melted sample exists in two different structures, which was explained in NMR investigations. One of them, that is isomer *E,Z*, is thermodynamically less stable and after heating converts into the *E,E* isomer and slow cooling prevents formation of this structure. During rapid cooling from the melt the both structures are created.

DSC thermogram of the polymers poly(AZ1) and poly(AZ2) were very similar. During first heating run (20 °C/min) glass transition was detected at 115 °C and 121 °C for poly(AZ1) and poly(AZ2), respectively. Then exothermic peak starting at about 280 °C with maximum at about 350 °C and with the end at about 400 °C was observed for the both polymers. Fig. 3c shows DSC of the poly(AZ1) as an example. It is interesting that the residues of the samples after heating to 400 °C were about 76–77% for the both polymers. It seems to indicate that during heating any volatile products were evolved. It should be noted that no residues after heating to 400 °C of model compounds AZ1 and AZ2 were found – the samples were entirely decomposed. Freche et al. [16] described that during heating of some azines, evolution of nitrogen with formation of ethylene unit was observed. FTIR spectra of the both polymers residues after heating to 400 °C, exhibited band at 807 cm⁻¹ indicating the presence of C–S linkage, wide band in the range of 1000–1500 cm⁻¹ which can confirm the presence of –CH=CH– bonds in thiophene ring and as ethylene units and the band at 2215 cm⁻¹ characteristic for –C≡N group. In Fig. 4. FTIR spectra of the polymer poly(AZ1) and its residue after heating to 400 °C are shown as an example.

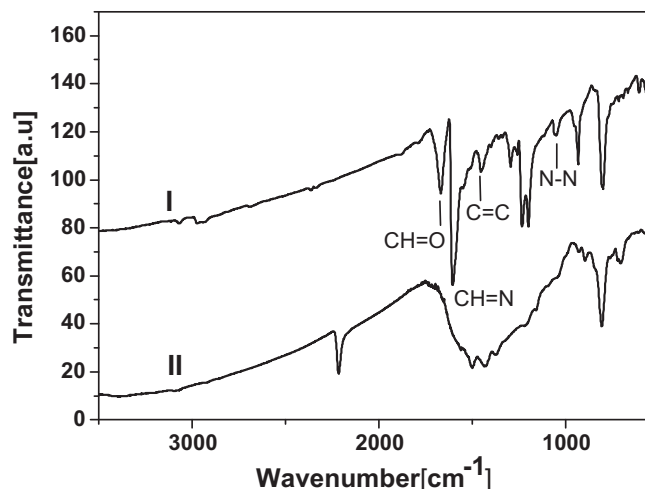


Fig. 4. FTIR spectra of poly(AZ1) before (I) and after heating to 400 °C (II).

Elemental analysis of the poly(AZ2) residue revealed the following contents of the carbon, hydrogen and nitrogen atoms as 48.53%, 2.27% and 5.88%, respectively. Taking into account the given results of infrared spectroscopy and elemental analysis it can be concluded that thermal decomposition of the polyazines with the thiophene units could proceed on different pathways not only with nitrogen evolution.

For the both polyazines thermogravimetric (TGA) analysis was performed. The polymers revealed similar thermal stability. The decomposition temperature based on 10% weight loss temperature (*T*₁₀), usually considered as the criterion in determining the thermal stability of polymers, was slightly lower for poly(AZ1) (321 °C) compared with poly(AZ2) (345 °C). The temperature of the maximum decomposition rate (*T*_{max}), as evidenced by the differential thermogravimetric (DTG) curves, was 338 °C and 345 °C for poly(AZ1) and poly(AZ2), respectively. It should be stressed that *T*₁₀ of poly(AZ1) is very close to *T*_{max} and is the same in the case of poly(AZ2). Furthermore, polymers exhibited excellent residual weights at 800 °C, in the range 44–49% which indicates good flame-retardant characteristics associated with these polymers. Taking into consideration TGA results it was found that at 400 °C residue of the polymers was about 78% and 84% correspondingly to the residues of the samples after heating to 400 °C in DSC analyses. Comparing the thermal stability of poly(AZ1) with the same polymer described in the literature [1b], it was found that our polyazine exhibited different thermal behaviour. Polymer presented in Ref. [1b] showed a weight loss ranging from 25 to 35% near 330 °C and definitively degraded at 700 °C (heating rate 5 °C/min.). Thus, poly(AZ1) is thermally more stable in relation to described polymer.

2.3. Optical properties

The optical properties, that is absorption and emission of the studied compounds were analysed by UV–vis and photoluminescence (PL) spectroscopy in solution and in the solid state as blends with poly(methyl methacrylate) (PMMA). The solvatochromic behaviour of the compounds in two solvents, namely NMP ($\epsilon = 33.00$) and chloroform ($\epsilon = 4.81$), with a different dipole moment and consequently with a different polarity, was studied. Additionally, the UV–vis and PL properties of the compounds before and after protonation with HCl and doping with FeCl₃ were tested. The spectra of doped compounds were measured after the addition of 100 μ L of dopant water solution of concentration 3×10^{-4} M to 3 mL of compound solution in NMP of concentration 1×10^{-5} M.

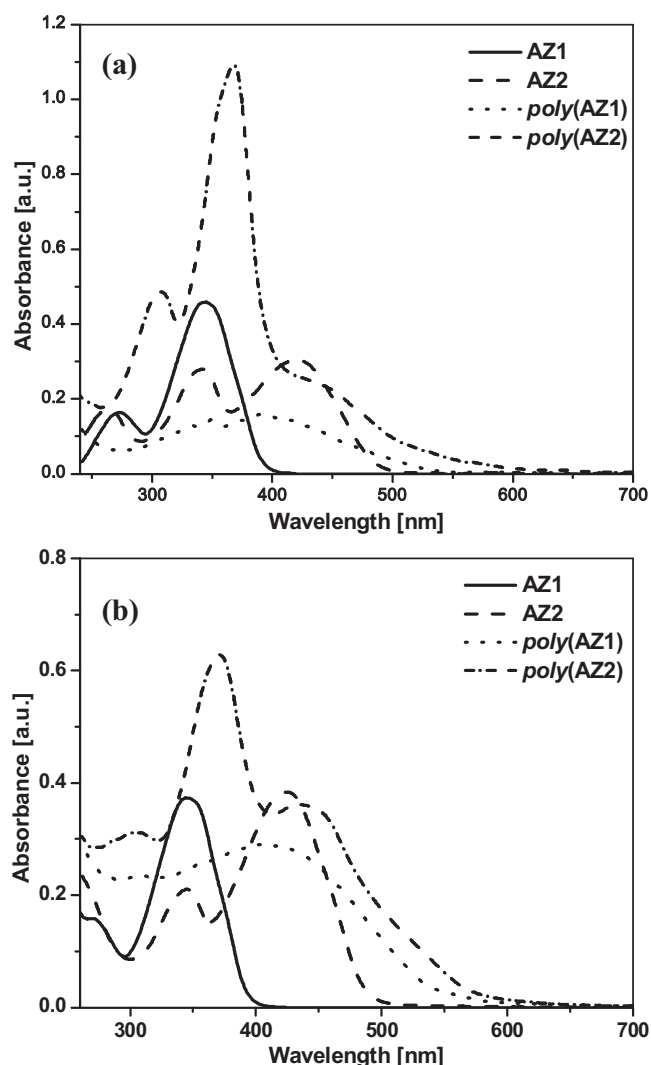


Fig. 5. UV-vis absorption spectra of investigated compounds in (a) chloroform and (b) NMP solution. Solution concentration of AZ1 and AZ2 was 1×10^{-5} M.

2.3.1. UV-vis absorption properties

The UV-vis absorbance spectra of studied azines and polyazines in chloroform and NMP solution are shown in Fig. 5, whereas their absorption spectra data are summarized in Table 2.

In the case of polyazines only qualitative measurements were carried out because of low solubility of these polymers. Electronic spectra of investigated compounds exhibited broad absorption band in the range from 240 nm to 650 nm (polyazines) and 550 nm (azines) with two or three maxima, dependent on the chemical constitution of the compound, which are clearly structured (except for *poly*(AZ1)). Absorption in NMP solution showed expected red shifted maxima in azines relative to the starting thiophene and bithiophene aldehydes (289 nm and 370 nm, respectively). This is due to the extended conjugation through azine bonds. The overall shift from thiophene and bithiophene aldehydes to AZ1 and AZ2 is practically the same (about 56 nm). In solution AZ1 and the corresponding polymer *poly*(AZ1) exhibited two absorption maxima (λ_{\max}), whereas AZ2 and *poly*(AZ2) exhibited additional absorption maximum at lower energy region. The introduction of second thiophene ring into compounds influenced significantly their UV-vis absorption properties, that is extended bathochromically the range of absorption. The absorption spectra of the polyazines are bathochromically shifted (50 nm for *poly*(AZ1) and 19 nm for *poly*(AZ2)) with respect to the spectra of model compounds which

is a consequence of the increased conjugated π -electron system of polymers in comparison with low molecular compounds (cf. Table 2). It proves that conjugated π -electron system did not remain intact during polymerization reaction. The effect of solvent polarity on UV-vis spectra was investigated. Solvatochromism arises from the interaction between the dipole moments of the solvent and the molecule. As a result, solvatochromism appears to a large effect if the difference in the dipole moments at the ground state and the excited state is large [17]. Despite the different polarity of the applied solvents, the spectra of azines recorded in NMP and chloroform showed a λ_{\max} position at almost the same wavelength what means that the solvatochromic effect is not observed. On the other hand, polyazines are more sensitive to solvent polarity, especially the absorption band at longer wavelength. In the case of polyazines hypsochromic shift (13–41 nm) was observed considering a λ_{\max} position in NMP and chloroform solution (cf. Table 2). A hypsochromic shift of the absorption band, with increasing solvent polarity is usually called “negative solvatochromism” [17]. It means that with increasing solvent polarity, the ground-state molecule is better stabilized by solvation than the molecule in the excited state. Thus, larger differences in dipole moment at ground states and the excited states are observed in polyazines than in model compounds.

In the solid state, as blend with PMMA, changes in the absorption spectra based on the λ_{\max} position and the shape of the absorption bands were observed in comparison with the solution. Namely, absorption band with weakly structured maximum is hypsochromically shifted (except for AZ1) in relation to solution (cf. Table 2). However, the conformation of the compounds can be different in dependence on the surrounding.

2.3.2. Photoluminescence properties

Many factors can influence the photoluminescence (PL) properties of organic compounds mainly arising directly from chemical structure as well as from experimental conditions. In this work the influence of three factors on the emission spectra was considered: (i) changing the excitation wavelength, (ii) changing the kind of solvent, and (iii) blending the light-emitting compound with a nonemissive polymer (PMMA).

The emission spectra of azines were recorded with different excitation wavelengths in solutions at concentration 1×10^{-5} M. The concentration of polymers in solution was approximately 1×10^{-5} M. Moreover, acquisition of the PL spectra of the studied compounds in NMP and chloroform solutions, that is, in solvents that differed in polarity, allowed analysing the solvent effect on PL properties.

In the first step, solutions of the studied compounds were excited with excitation wavelengths (λ_{ex}) in the range of 330–450 nm. The influence of the excitation wavelength on PL properties, that is on the position of emission band maximum (λ_{em}) and intensity of emitted light for AZ2 as example is presented in Fig. 6a, while the emission spectral data of studied compounds are summarized in Table 3.

The investigated compounds under different excitation wavelengths (λ_{ex}) exhibited a single emission band, with the maximum (λ_{em}) located in the blue or green region. For all the compounds an increase of excitation wavelength causes a shift of the emission maximum towards higher wavelengths and the lowest PL intensity was obtained under λ_{ex} from 400 to 450 nm (except for AZ1 in CHCl_3 solution). In the case of polyazines the highest PL intensity independently on kind of solvent was found under $\lambda_{\text{ex}} = 370$ and 340 nm for *poly*(AZ1) and *poly*(AZ2), respectively. Solvent polarity is another factor that should affect the emission spectra. The maximum of emission is expected to be bathochromically shifted in solvent with higher dielectric constant. This phenomenon, that is, the red shift of λ_{em} in more polar NMP in comparison with less polar chloroform is seen for polyazines (except for *poly*(AZ1) under

Table 2The results of UV–vis measurements of the starting azines ($c = 1 \times 10^{-5}$ M) and polyazines, and doped with HCl and FeCl₃ and as solid state as blend with PMMA.

Code	CHCl ₃ ($\epsilon = 4.81$) ^b		NMP ($\epsilon = 33.00$) ^b		Doped with HCl	Doped with FeCl ₃	In solid state ^a
	λ_{\max} [nm]	ϵ [l mol ⁻¹ cm ⁻¹]	λ_{\max} [nm]	ϵ [l mol ⁻¹ cm ⁻¹]	λ_{\max} [nm]	λ_{\max} [nm]	λ_{\max} [nm]
AZ1	273	14,430	270	11,630	342	268	371 ^c
	343	40,410	346	27,430		345	
AZ2	263	17,890	345	17,590	341	342	377 ^c
	341	28,600	425	32,090	427	427	
	429	31,180					
poly(AZ1)	350	–	309	–	405	407	371 ^c
	393	–	406	–			
poly(AZ2)	307	–	304	–	369	371	371 ^c
	367	–	370	–	434	434	
	448	–	434	–			

^a Blend with PMMA concentration = 1% of compound in blend.^b ϵ : dielectric constant.^c The position of absorption band calculated using the second derivatives method (i.e., the minimum of the second derivative of absorption corresponds to the absorption maximum) and for such band ϵ was not calculated.

$\lambda_{\text{ex}} = 450$ nm and *poly*(AZ1) under $\lambda_{\text{ex}} = 330$ nm). However, in the case of azines negative solvatochromism is detected (cf. Table 3). The significant influence of solvent polarity was detected considering PL intensity. Both azines and polyazines exhibited much higher PL intensity in NMP solution (cf. Fig. 6b–e). Additionally, the fluorescence characteristics of obtained compounds in solid state as blend with PMMA were studied. The maxima of emission in blends containing about 1% of azines and polyazines are presented in Table 3. Fig. 6f shows the exemplary PL spectrum of AZ2 in solution and in blend. The highest PL intensity for blends was detected under $\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{ex}} = 370$ nm for AZ2. Taking into account the λ_{em} position in blend and NMP solution, hypsochromic shift is observed in solid state in relation to solution, except for AZ1. Azines emitted light with the highest PL intensity with λ_{em} position hypsochromically shifted (about 52 and 16 nm) compared with polyazines. It confirms the better conjugation in the case of polymers. The effect of the number of thiophene rings on PL properties is not the same in azines and polyazines. It was found that azine with bithiophene structure (AZ2) emitted light with the highest intensity with λ_{em}

position bathochromically shifted in relation to AZ1 both in NMP solution and in blend. On the other hand, λ_{em} position of polyazine with bithiophene rings (*poly*(AZ2)) was blue shifted (24 nm in NMP solution and 3 nm in blend) in comparison with *poly*(AZ1). All investigated compounds emitted blue light with the highest intensity.

2.3.3. Characterization of doped azines and polyazines

The presence of lone electron pair of the nitrogen atom in obtained compounds creates opportunity for modification of optical properties by supramolecular concept, which is doping method. The use of noncovalent interactions is a crucial synthetic tool due to its great potential in the design of new materials [18]. It is well known that compounds with imine bonds are capable of protonation and complexation. It is expected that doping influence the better conjugation in the polymer chain. However, to the best of our knowledge only in one paper doping with iodine of polyazines experiment has been described and significant increase of the conductivity was demonstrated [1a]. In this work hydrochloric acid and ferric chloride were used as protonation and complexation agents,

Table 3

Photoluminescence data of investigated azines and polyazines under different excitation wavelength.

Code	Medium	PL λ_{\max} [nm]			λ_{ex} [nm]			
		330	340	360	370	400	430	450
AZ1	NMP ^a	406	406	434	455	485	492	518
	CHCl ₃ ^a	454	450	454	456	456	–	–
	Blend ^b	408	415	448	455	467	498	506
	NMP ^a + HCl	404	408	428	438	476	492	518
	NMP ^a + FeCl ₃	405;	406;	433;	479;	486	489	487;
		588	588	592	590			581
AZ2	NMP ^a	412	416	440	458	480	504	504
	CHCl ₃ ^a	458	458	452	472	478	496	522
	Blend ^b	405	414	435	449	460	490	500
	NMP ^a + HCl	426	428	440	442	468	492	516
	NMP ^a + FeCl ₃	412	429	436	442	468	494	518
<i>poly</i> (AZ1)	NMP	456	452	458	458	466	492	518
	CHCl ₃	432	438	442	432	451	–	518
	Blend ^b	405	412	436	438	461	496	–
	NMP + HCl	448	458	456	456	466	492	514
	NMP + FeCl ₃	455	454	458	458	454	492	516
<i>poly</i> (AZ2)	NMP	426	434	454	458	494	554	562
	CHCl ₃	426	424	438	428	474	–	–
	Blend ^b	402	408	430	431	460	–	–
	NMP + HCl	430	436	444	452	472	554	552
	NMP + FeCl ₃	428	429	443	450	459	550	556

Bold data indicates the most intense luminescence of compound.

^a $c = 1 \times 10^{-5}$ M.^b 1% polymer concentration.

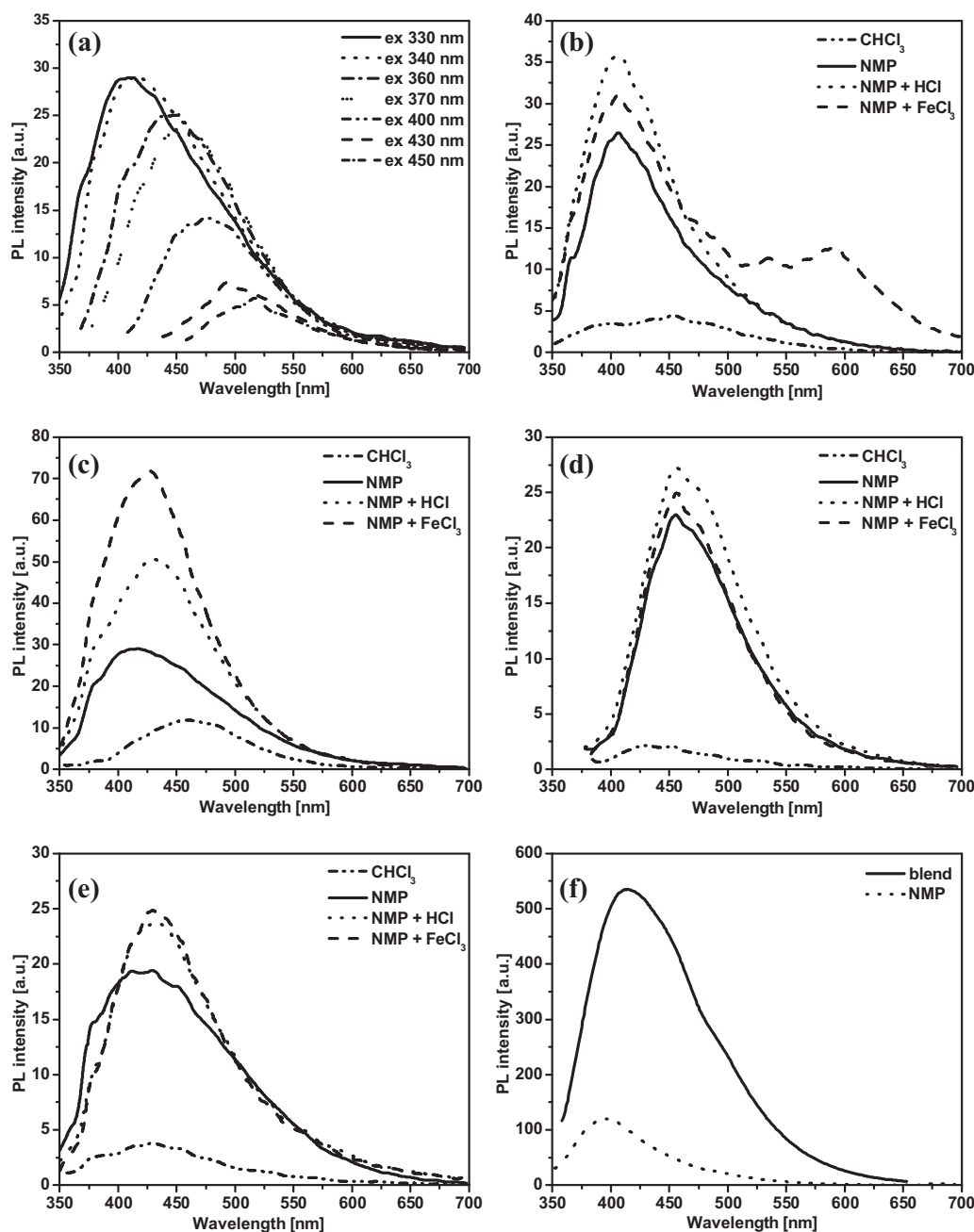


Fig. 6. The photoluminescent spectra of (a) the AZ2 under various excitation wavelengths in NMP solution (concentration 1×10^{-5} M), (b) AZ1 under $\lambda_{\text{ex}} = 330$ nm, (c) AZ2 under $\lambda_{\text{ex}} = 340$ nm, (d) *poly*(AZ1) under $\lambda_{\text{ex}} = 370$ nm, (e) *poly*(AZ2) $\lambda_{\text{ex}} = 340$ nm in NMP and CHCl_3 solutions and after doping with HCl or FeCl_3 and (f) AZ2 in NMP solution and in blend with PMMA under $\lambda_{\text{ex}} = 340$ nm.

respectively, in the mole ratio of dopant to compound being 1:1 with respect to the imine nitrogen in NMP solution. As far as we are aware, this is the first example of doping the compounds containing hydrazone linkages with HCl and FeCl_3 . Doped azines and polyazines were subjected to UV–vis and PL spectroscopy. The lack of influence on λ_{max} position between the starting and doped compounds was observed (cf. Table 2). However, decrease in absorption intensity after adding HCl and FeCl_3 into azines was noticed in contrary to polyazines, in which slightly increase of absorbance was found. The PL spectra of the doped compounds under the λ_{ex} which gave the best PL intensity are collected in Fig. 6b–e. It is expected that doping could influence both the emission wavelength and intensity of the photoluminescence [19]. Taking into consideration the λ_{em} position before and after protonation with HCl and

complexation with FeCl_3 , only in the case of AZ2 the bathochromic shift was observed, which confirms the better conjugation of doped azine. On the other hand, in all cases the investigated doped compounds exhibited increasing PL intensity compared with starting compounds.

2.4. Electrochemical and spectroelectrochemical properties

Electrochemical properties of each compound were investigated in MeCN solution with the aid of 0.1 M Bu_4NPF_6 as the supporting electrolyte, by means of cyclic voltammetry (CV) and differential pulse voltammetry (DPV). All established parameters are enclosed in Table 4 and in Fig. 7. DPV voltammograms of all

Table 4Redox potentials, HOMO and LUMO energies and electrochemical band gaps (E_g) of azines and polyazines.

Code	AZ1	AZ2	poly(AZ1)	poly(AZ2)	E-poly(AZ2)
E_{red1} (onset, CV)	−1.78	−1.83	−1.19	−1.37	−1.55
E_{red2} (onset, CV)	–	–	−1.30	−1.52	–
$E_{1/2red1}$	−1.90	−1.92	−1.27	−1.44	−1.60
$E_{1/2red2}$	–	–	−1.38	−1.59	–
E_{red} (onset, DPV)	−1.67	−1.89	−1.14	−1.36	–
E_{ox} (onset, CV)	1.32	0.62	0.86	0.55	0.30
E_{ox} (onset, DPV)	1.40	0.72	1.03	0.58	–
E_g (CV)	3.10	2.45	2.05	1.92	1.85
E_g (DFT)	3.50	2.82	–	–	–
HOMO (CV)	−6.12	−5.42	−5.66	−5.35	−5.10
HOMO (DFT)	−5.63	−5.15	–	–	–
LUMO (CV)	−3.02	−2.97	−3.61	−3.43	−3.25
LUMO (DFT)	−2.04	−2.33	–	–	–

Measured in CH_3CN solution, $E_{1/2red}$, formal redox potential calculated as $(E_{ox} + E_{red})/2$ from cyclic voltammetry (CV), $E_g = E_{ox}$ (onset) $- E_{red}$ (onset), HOMO = $-4.8 - E_{ox}$, LUMO = $-4.8 - E_{red}$.

investigated compounds are also collected in Fig. 8a, whereas CV voltammograms are collected in Fig. 3S in Supporting Information.

Firstly, electrochemical properties of the model compounds, namely AZ1 and AZ2, were investigated. For AZ1 the reduction is a one-step process (−1.67 V peak onset) and is a quasi-reversible in nature (peak-to-peak separation > 100 mV). The oxidation on the other hand is an irreversible E_{rC} process, however, in this case the polymerization does not occur (probably due to the fact that the polymerization potential is higher than the degradation one). The other model compound – AZ2 – exhibits a reversible reduction at the potential as high as −1.89 V (peak-to-peak separation = 70 mV). On the contrary to AZ1, the oxidation of AZ2 is followed by electropolymerization, what is presented in Fig. 8b. The structure of polyazine (E-poly(AZ2)) obtained by electropolymerization of AZ2 is presented in Fig. 1. The voltammogram is closely related to the one recorded by Tindale et al. [3b] for 1,4-dimethyl-1,4-bis(2,2'-bithien-5-yl)-azine (BT-azine). However, the authors do not reveal the reference system used for the measurements, making it therefore unable to thoroughly compare the obtained results. E-poly(AZ2) exhibited reversible peak at 0.30 V (cf. Table 4), what is attributed to the oxidation of the quaterthiophene moieties formed [20] in contrast to BT-azine. Comparing AZ1 and AZ2 in detail, a few findings can be made. The exchange of the thiophene ring for the bithiophene causes a substantial lowering of the oxidation potential from 1.4 V to 0.7 V, for AZ1 and AZ2, respectively. It is a direct consequence of significantly better stabilization of the cation radical species (located on the thiophene moiety) formed during the oxidation in AZ2. The magnitude of this phenomenon is so high that the electropolymerization of AZ2 becomes possible, in contrast to AZ1. What is more, bithiophene is a far stronger donor than thiophene, therefore the electron density on the azine group is enhanced, what results in the lowering of the reduction potential from −1.78 V (thiophene model) to −1.83 V (bithiophene model). Polyazines exhibit two fully reversible reduction steps. In the case

of poly(AZ1), their maxima are separated by 80 mV, making it therefore hard to make out on CV. The separation of these two peaks is much better recorded on DPV, according to higher sensitivity of this method. The peak onset for the two reduction steps is as follows: $E_{red1} = -1.14$ V and $E_{red2} = -1.22$ V. Similarly as for AZ1, the oxidation (1.03 V) of poly(AZ1) is an irreversible process. The reduction of poly(AZ2) is also a two-step process with reduction potentials being as high as $E_{red1} = -1.36$ V and $E_{red2} = -1.50$ V. However, in the case of poly(AZ2) both reduction and oxidation (peak onset = 0.58 V) are fully reversible processes (cf. Fig. 8c). It is logical to assume that the aforementioned findings concerning the lowering of the oxidation potential in case of the model compounds is transferred to the polymeric conditions. The bithiophene moiety again substantially lowers the oxidation potential from 1.03 V for poly(AZ1) to 0.58 V for poly(AZ2). However, it also affects the reduction potential, making it more difficult, because of its donating character. Therefore, the reduction occurs at lower potential (−1.36 V) in comparison with −1.14 V from bithiophene analogue. The electrochemical oxidation and reduction onset potentials were used for estimation of HOMO and LUMO energies (or rather, ionization potentials and electron affinities) of the materials, assuming the IP of ferrocene to be equal to −4.8 eV. The calculated HOMO, LUMO levels together with electrochemically energy band gap (E_g) are presented in Table 4 and Fig. 7. The presence of quaterthiophene structure in E-poly(AZ2), that is polymer obtained by electropolymerization of AZ2 leads to higher laying HOMO level in relation to polymer with thiophene or bithiophene in repeating polymer units. Moreover, E-poly(AZ2) exhibited the highest value of LUMO level compared with poly(AZ1) and poly(AZ2). The values of E_g of the compounds were ranked in the order by CV: AZ1 > AZ2 > poly(AZ1) > poly(AZ2) > E-poly(AZ2). Polymers exhibited higher E_g as related to their model compounds. Azine and polyazine with bithiophene showed lower value of E_g in comparison with compounds with thiophene ring.

Spectroelectrochemical measurements were conducted in thin films deposited on ITO (indium-tin oxide) in acetonitrile and with the aid of 0.1 M Bu_4NPF_6 as the supporting electrolyte. No changes to the progression of the UV-vis spectrum in the range of 300–1000 nm were indicated during the reduction of AZ1 and AZ2. These results may suggest that the reduction is associated with the part of the molecule (the azine) that does not absorb light in the aforementioned wavelength range. On the other hand, the oxidation of AZ2 brings many differences to the progression of the UV-vis spectrum. As it has been mentioned previously in the electrochemical paragraph, this compound undergoes electropolymerization under these conditions. After setting the potential at 1.16 V for 30 min, so that the polymerization was complete, the band associated with the absorption of the bithiophene rings (with three maxima) turns into one broad red-shifted band (cf. Fig. 4S in Supporting Information). During the reduction of poly(AZ1) a hyperchromic effect of the broad band between 400 and 500 nm may be distinguished, along with the hypochromic shift of the band between 550 and 800 nm (cf. Fig. 4S in Supporting Information). In the case of poly(AZ2) reduction resulted in appearance

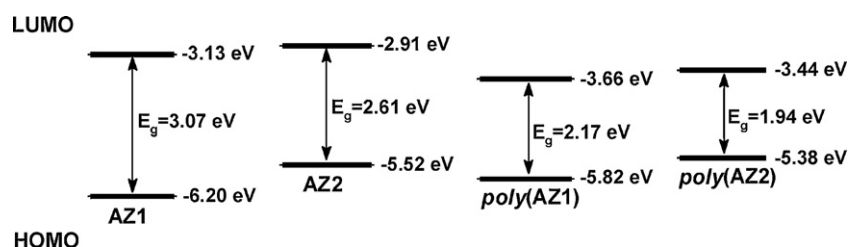


Fig. 7. Simple energy level diagram of the calculated HOMO, LUMO levels and energy band gaps of obtained azines and polyazines determined by differential pulse voltammetry (DPV).

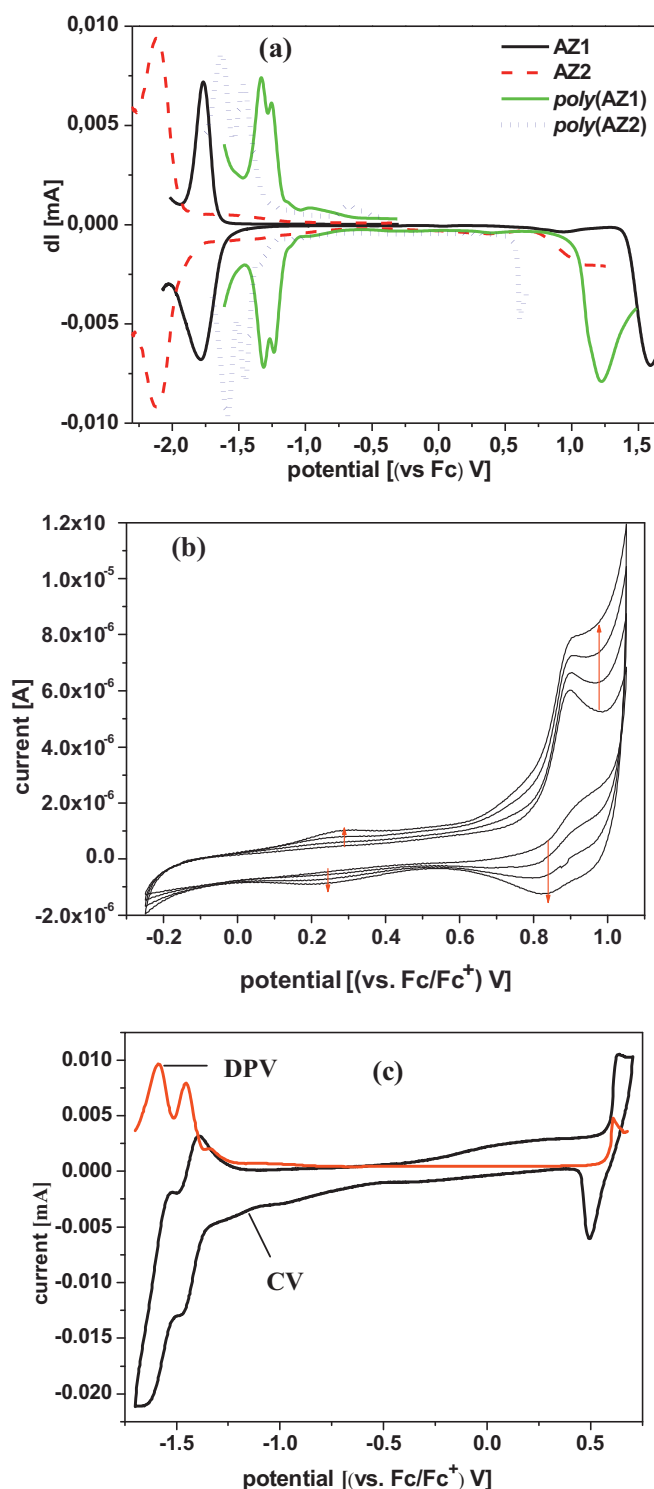


Fig. 8. (a) Differential pulse voltammograms (DPV) in acetonitrile containing 0.1 M $n\text{Bu}_4\text{PF}_6$, with a step potential of 2.5 mV, (b) cyclic voltammograms of 1 mM solution of (AZ2) during polymerization; Pt electrode as working electrode; scan rate of 100 mV s^{-1} ; 1 mM monomer solutions in 0.1 M $n\text{Bu}_4\text{PF}_6/\text{MeCN}$ (only scans 1, 5, 9 and 13 are shown for clarity), (c) cyclic voltammogram (CV, black lines) of ($\text{poly}(\text{AZ2})$) in acetonitrile containing 0.1 M $n\text{Bu}_4\text{PF}_6$ at a scan rate of 100 mV s^{-1} . The red line is a differential pulse voltammogram with a step potential of 2.5 mV. The measurements were performed using a platinum working electrode, and referenced against $\text{Cp}_2\text{Fe}^{+/0}$ couple. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

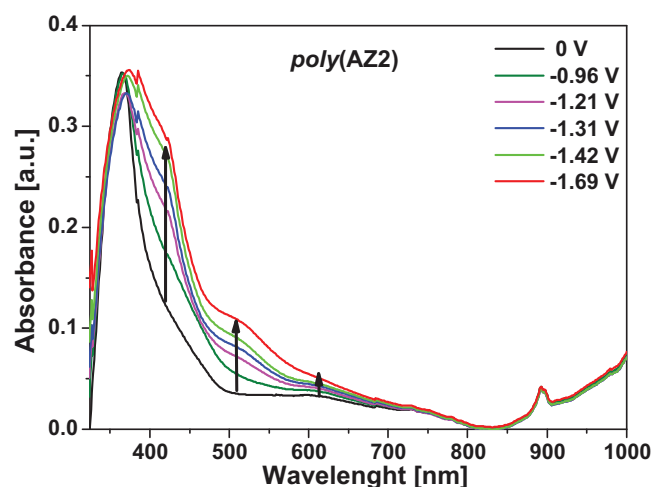


Fig. 9. UV-vis spectra recorded in situ during the cathodic reduction of polymer film ($\text{poly}(\text{AZ2})$) on ITO electrode in 0.1 M $n\text{Bu}_4\text{PF}_6$ solution in MeCN.

of new band at 510 nm and increase of the band intensity at 420 nm and 620 nm (cf. Fig. 9).

2.5. Theoretical calculations

DFT calculations were carried out using B3LYP functional combined with 6-31G(d,p) basis set for obtained azines and polyazines. Additionally, for $\text{poly}(\text{AZ1})$ and $\text{poly}(\text{AZ2})$ theoretical calculations were carried out using approach suggested by Bendikov and Zade [21], where the band gap of the polymers is extrapolated as a function of the reciprocal number of unit cells in the oligomer backbone, and from Periodic Boundary Conditions, implemented in Gaussian09 [22]. For the model compounds AZ1 and AZ2 optimized geometries together with the frontier Kohn–Sham orbital projections are enclosed in Fig. 10a.

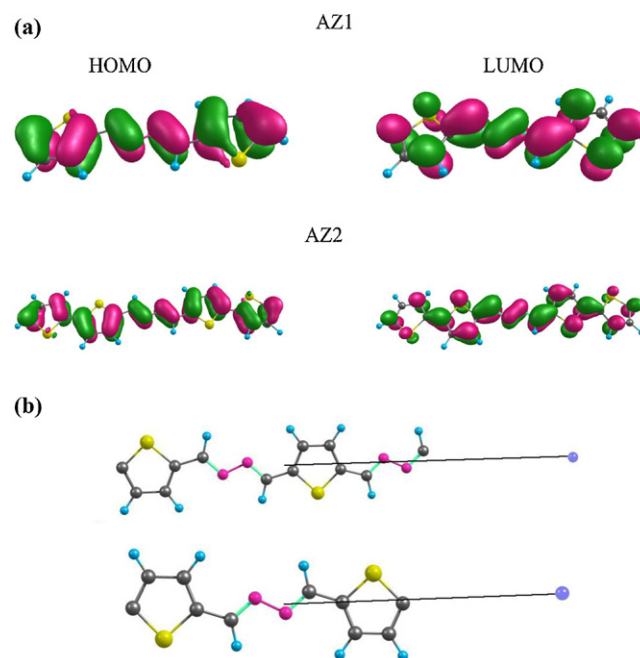


Fig. 10. (a) Kohn–Sham orbital plots of the model compounds AZ1 and AZ2; (b) unit cells for polymers together with the translation vectors derived from PBC calculations.

Table 5

Frontier crystal orbital energies together with the corresponding band gap (E_g) derived from PBC calculations and E_g approximated in an oligomeric approach.

Code	<i>poly</i> (AZ1)	<i>poly</i> (AZ2)
HOCO [eV]	−5.31	−5.04
LUCO [eV]	−3.15	−2.96
E_g [eV]	2.15	2.09
E_g (linear) ^a	1.89	1.81
E_g (quadratic) ^a	1.91	1.88

^a E_g approximated in an oligomeric approach.

The HOMO and LUMO are in both cases delocalized over the whole molecule, without any substantial localization on either azine or thiophene moiety. This finding stays in contrast with the spectroelectrochemical measurements, where the reduction is associated exclusively with the azine moiety. This contradiction may be explained by fact that density functional theory usually tends to strongly delocalize electron density. Similar results were observed for example when EPR and theoretical results were taken into consideration together [25]. A description of the frontier molecular orbitals of AZ1 and AZ2 is gathered in Table 4. As can be seen, the DFT calculations slightly overestimates the HOMO/LUMO values and as consequence the E_g value, however, the relative position of the frontier molecular orbital (FMO) energies is retained. The E_g values of AZ1 and AZ2 theoretically calculated are overestimated compared with DPV measurements by 0.52 eV and 0.22 eV, respectively. As was mentioned, *poly*(AZ1) and *poly*(AZ2) were examined using two different approaches. Firstly, the two species were examined on PBC/B3LYP/6-31G(d,p) level of theory providing with the HOCO and LUCO values, that is the highest occupied crystal orbital energy and the lowest unoccupied crystal orbital energy and also the band gap derived from them. The results of these calculations together with the unit cell used for the calculations are gathered in Table 5 and in Fig. 10b.

Secondly, for further insight into the band gap of the polymers the oligomeric approach was used. In this case the number of the cell units (n) was being elongated one by one up to 13 for *poly*(AZ1) and 9 for *poly*(AZ2). For each oligomer the HOMO–LUMO gap was derived and then it was plotted against the reciprocal number of n . The extrapolation of the $1/n$ to 0 resulted in an infinite cells number and therefore the band gap of the desired polymer. One important thing already put forward by Bendikov and Zade [21] is the convergence of the band gap with increasing of the n number. For small value of n the relationship is linear, however, for a specific value the extrapolation is much better resembled as a quadratic equation.

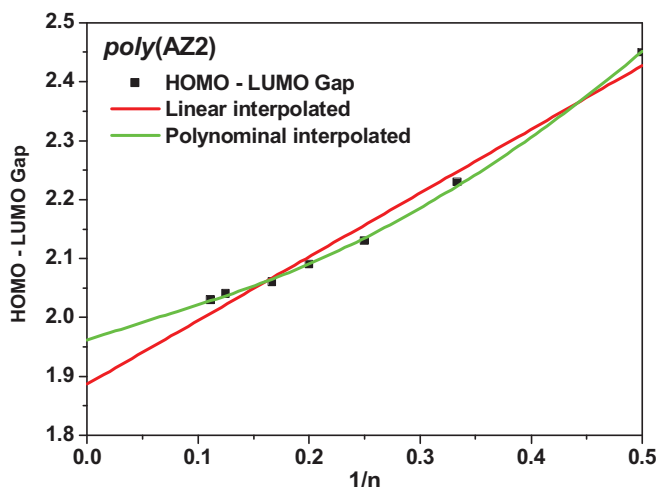


Fig. 11. Band gap convergence in *poly*(AZ2) obtained in the oligomeric approach.

These two things were taken into consideration and the resulted band gaps derived from all four extrapolations are given in Table 5 and is presented as example for *poly*(AZ2) in Fig. 11 (for *poly*(AZ1) cf. Fig. S5 in Supporting Information).

The values of the band gap obtained in both approaches, that is periodic boundary conditions and the extrapolation from the oligomers, are slightly different by 0.2–0.3 eV. However, they correspond very accurately with the values provided experimentally by CV and DPV and reveal that both methods may be used together for band gap simulations of materials to be synthesized, as already mentioned by Bendikov and Zade [21]. The differences between the theoretical and experimental result from dynamic processes along the polymer backbone, which simple DFT calculations do not resemble [23].

3. Experimental

3.1. Materials

2-Thiophenecarboxyaldehyde, 2,2'-bithiophene-5,5'-dicarboxyaldehyde, 2,5-thiophenedicarboxyaldehyde, hydrazine monohydrate 98%, N-methyl-2-pyrrolidinone (NMP), ethanol and acetic acid (99.5%) were purchased from Aldrich Chemical Co.

2,2'-bithiophene-5,5'-dicarboxyaldehyde was prepared according to procedure [24] (^1H NMR (CDCl_3 , ppm): δ 7.43 (d, $J=4.0$ Hz, 2H), 7.74 (d, $J=4.0$ Hz, 2H), 9.92 (s, 2H); m.p. 214 °C (lit. m.p. 215–216.5 °C) [24]).

3.2. Synthesis of model compounds

Into aldehyde: 2-thiophenecarboxyaldehyde (0.6168 g; 5.5 mmol) or 2,2'-bithiophene-5,5'-dicarboxyaldehyde (1.0681 g; 5.5 mmol) dissolved in 3 mL of ethanol, solution of hydrazine (0.1277 g; 2.5 mmol) in 2 mL of ethanol was added dropwise and then 2 drops of acetic acid were added. After a few seconds yellow product started to precipitate. The reaction mixture was stirred for 2 h at room temp. The precipitant was filtrated, washed several times with ethanol and dried at 50 °C in vacuum for 2 days. Hydrazine condensed with 2-thiophenecarboxyaldehyde yielded compound AZ1 and with 2,2'-bithiophene-5-carboxyaldehyde gave compound AZ2.

AZ1: Yellow powder. Yield: 83%. m.p. = 161 °C (lit. 151–152 °C [14c], 148–149 °C [14b]); ^1H NMR (400 MHz, CDCl_3) δ 8.78 (s, 2H, CH=N), 7.48 (dt, $J=5.0$, 1.0 Hz, 2H), 7.42 (dd, $J=3.7$, 1.0 Hz, 2H), 7.12 (dd, $J=5.0$, 3.7 Hz, 2H); ^{13}C NMR (400 MHz, CDCl_3) δ 155.91 (CH=N), 139.15, 132.51, 130.15, 127.95; FTIR (cm^{-1}): 1608 (C=N stretching), 1420 (C=C in thiophene ring), 1040 (N–N stretching); elemental analysis calcd. (%) for ($\text{C}_{10}\text{H}_8\text{N}_2\text{S}_2$) (220.92): C 54.51, H 3.66, N 12.71; found C 54.50, H 3.47, N 12.70.

AZ2: Orange powder. Yield: 75%. m.p. = 163, 205 °C (lit. 191–192 °C [14c]); FTIR (cm^{-1}): 1610 (C=N stretching), 1451 (C=C in thiophene ring), 1059 (N–N stretching); elemental analysis calcd. (%) for ($\text{C}_{18}\text{H}_{12}\text{N}_2\text{S}_4$) (384.57): C 56.22, H 3.14, N 7.28; found C 56.44, H 3.27, N 7.40. It was found that azine AZ2 precipitate after reaction consists of two isomers:

AZ2 *E,E* isomer: ^1H NMR (400 MHz, CDCl_3) δ 8.70 (s, 2H CH=N), 7.31 (d, $J=3.9$ Hz, 2H), 7.29 (d, $J=4.4$ Hz, 4H), 7.18 (d, $J=3.8$ Hz, 2H), 7.08–7.03 (m, 2H). ^{13}C NMR (400 MHz, CDCl_3) δ 155.39 (CH=N), 141.84, 137.50, 136.90, 133.29, 128.14, 125.76, 124.99, 124.09.

AZ2 *E,Z* isomer: ^1H NMR (400 MHz, CDCl_3) δ : 8.64 (s, 1H), 8.09 (s, 1H), 7.39 (d, $J=3.9$ Hz, 1H), 7.37–7.33 (m, 4H), 7.31 (d, $J=3.8$ Hz, 1H), 7.22 (d, $J=3.9$ Hz, 1H), 7.17 (d, $J=3.8$ Hz, 1H), 7.10 (dd, $J=5.2$, 3.6, Hz, 1H), 7.10 (dd, $J=5.2$, 3.6, Hz, 1H). ^{13}C NMR (400 MHz, CDCl_3) δ : 153.75 (CH=N), 150.96 (CH=N), 142.85, 141.88, 137.94, 137.20,

134.65, 133.76, 133.32, 132.30, 128.19, 128.16, 125.87, 125.80, 125.09, 124.69, 124.24, 122.81.

3.3. Synthesis of polymers

Hydrazine (1 mmol, 0.051 g) in 2 mL of NMP was added dropwise to dialdehyde: 2,5-thiophenedicarboxaldehyde (1 mmol, 0.1402 g) or 2,2'-bithiophene-5,5'-dicarboxaldehyde (1 mmol, 0.2223 g) dissolved in 2 mL of NMP and then a few drops of acetic acid were added. The mixture became red and small amount of precipitate occurred. Additional 4 mL of NMP was added and the mixture was stirred and heated at 60 °C for 3 h and then overnight at room temp. Then the mixture was poured into 40 mL of methanol and resulting precipitate was filtered, washed several times with methanol and dried in vacuum at 50 °C. Hydrazine condensed with 2,5-thiophenedicarboxaldehyde resulted in polymer *poly(AZ1)* [1b] and with 2,2'-bithiophene-5,5'-dicarboxaldehyde gave polymer *poly(AZ2)*.

poly(AZ1): Red powder. Yield: 78%. FTIR (cm⁻¹): 1667 (CH=O), 1603 (CH=N stretching), 1453 (C=C in thiophene ring), 1049 (N–N stretching). Anal. Calcd. for (C₆H₄N₂S) (136.12): C 52.94, H 2.94, N 20.58; found C 55.26, H 3.46, N 19.50.

poly(AZ2): Brown powder. Yield: 80%. FTIR (cm⁻¹): 1684 (CH=O), 1602 (CH=N stretching), 1431 (C=C in thiophene ring), 1062 (N–N stretching). Anal. Calcd. for (C₁₀H₆N₂S₂) (218.18): C 55.05, H 2.77, N 12.84; found C 50.59, H 3.09, N 12.30.

3.4. Measurements

Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker AC 400 MHz spectrometer using chloroform (CDCl₃) as solvent and TMS as the internal standard. Differential scanning calorimetry (DSC) was performed with a TA-DSC 2010 apparatus (TA Instruments, Newcastle, DE, USA), under nitrogen using aluminium sample pans. Elemental analyses were performed using Perkin Elmer Analyzer 2400. FTIR spectra were recorded on a BIO-RAD FTS 40 A Spectrometer using KBr pellets. UV–vis absorption spectra were recorded in solution 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. Cyclic and differential pulse voltammetry experiments were conducted in a standard one-compartment cell, in dichloromethane (Carlo Erba, HPLC grade), under argon. 0.2 M Bu₄NPF₆ (Aldrich, 99%) was used as the supporting electrolyte. Theoretical DFT calculations were carried out using Gaussian09 package [21]. Geometries of the ground states of the model compounds and oligomeric species were fully optimized at B3LYP/6-31G(d,p) level of theory, while for polymer unit cells PBC/B3LYP/6-31G(d,p) level of theory was applied.

3.5. Blend preparation

Blends were obtained by dissolving the desired amount of compounds and PMMA in NMP to form a homogeneous solution (1%, v/v, concentration of compound in PMMA). Films cast on glass were dried in vacuum oven at 90 °C over 10 h.

4. Conclusions

In conclusion, azines and polyazines containing thiophene and bithiophene units were synthesized and characterized. The study revealed the clearly pronounced effect of the number of thiophene

rings on optical and redox properties of both types of investigated compounds. Bathochromic shifts for the absorption spectra were observed for compounds with bithiophene. Independently of the chemical structure, the obtained compounds emitted blue light. It was found that azine with bithiophene can be converted into polymer by electropolymerization, which is impossible in the case of azine with one thiophene ring. Presence of bithiophene units which are more electron-rich leads to higher lying HOMO levels about 0.68 eV for azines and 0.44 eV for polyazines. On the other hand, the value of LUMO level is lower, which results in decreasing of electrochemical energy gap from 3.07 to 2.61 eV for azines and from 2.17 to 1.94 eV for polyazines. The theoretically calculated *E_g* of polyazomethines very well corresponds to these obtained from experimental DPV measurements. Due to the reversible reduction process of polyazines they may be tested as charge transporting layers in optoelectronic devices. Moreover, the reversible oxidation and reduction confirm the polyazine with bithiophene and quaterthiophene units are both p- and n-dopable making these compounds suitable for advanced functional materials.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.synthmet.2012.06.019>.

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