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Article

Comparative Studies of Structural, Thermal, Optical and Electrochemical Properties of Azines with Different End Groups with Their Azomethine Analogues Towards Application in (Opto)Electronics

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Abstract: Two series of azines and their azomethine analogues were prepared via condensation reaction of benzaldehyde, 2-hydroxybenzaldehyde, 4-pyridinecarboxaldehyde, 2-thiophenecarboxaldehyde, and 4-(diphenylamino)benzaldehyde with hydrazine monohydrate and 1,4-phenylendiamine, respectively. The structures of given compounds were characterized by FTIR, ¹HNMR, and ¹³C NMR spectroscopy as well as elemental analysis. Optical, electrochemical, and thermal properties of all compounds were investigated by means of differential scanning calorimetry (DSC), UV-vis spectroscopy, stationary and time-resolved photoluminescence spectroscopy, and cycling voltammetry (CV).

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Additionally, the electronic properties, that is, orbital energies and resulting energy gap were calculated theoretically by density functional theory (DFT). Influence of chemical structure of the compounds on their properties was analyzed.

Keywords: diimines, imines, luminescence, HOMO and LUMO energy levels, DFT calculation

1. Introduction

Monodispersed π -conjugated compounds with well defined structures have drawn attention since many years as materials for a variety of electronic and optoelectronic devices such as light emitting diodes, photovoltaic cells and many others^{1,2}. Among them, azines, that is, N-N linked diimines (R-CH=N-N=CH-R) and azomethines having imine linkages (-CH=N-) and being easily synthesized, seem to be very interesting compounds. Additionally, their properties can be tuned by protonation with Lewis acids and complexation with Bronsted acids. Azines (diimines) are 2,3-diaza analogues of 1,3-butadiene and comprise a class of compounds that has been receiving increasing attention in recent years because of their utility in a number of interesting reactions and applications³ Azines have been utilized in bond formation reaction, polymerization, in the design of liquid crystals, and the synthesis of heterocyclic compounds^{4,5} Due to the presence of imine groups they are potential ligands and have been used as ligands in coordination chemistry^{6,7}. Azines are also considered as nonlinear optical materials⁸. Moreover, they can exhibit antibacterial, antifungal, antitumor activity^{4,9}. It was found that some of azines exhibit aggregation-induced emission enhancement (AIEE) characteristics, which is promising for applications in optical sensors, light emitting diodes, photovoltaic cells, and photoemitters¹⁰. It should be mentioned that only limited number of organic compounds have been reported do display AIEE characteristics. On

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the other hand azomethines are interesting alternatives to vinylene linkages and they are isoelectronic to their carbon counterparts and can be exploited for various applications¹¹⁻¹⁶. They as well exhibit high chemical, oxidative and reductive resistance and interesting photophysical properties^{17,18}.

In this work we prepare and investigate two series of azines and azomethines and comprehensively compare their selected properties. This research is the continuation of our efforts in the search of organic materials both polymers and low molecular weight compounds and for applications in organic (opto)electronics¹⁹⁻²⁴. In our previous work heterocyclic azine with thiophene rings¹⁹ and azomethine with TPA units²⁰ were described. Here, we report on synthesis of two series of symmetrical azines and azomethines in reaction of hydrazine or 1,4phenylenediamine with various aldehydes containing phenyl or hydroxyphenyl, or pyridine, or thiophene or triphenylamine (TPA) units and compare their spectral and electrochemical properties. While most of these compounds have been descried in literature, no comparative research focused on their optical and electrochemical properties has been carried out. To our best knowledge only one work describes the studies of photoluminescence and electrochemical properties of azomethines prepared from 1,4-phenylene diamine and benzaldehyde and 2-thiophenecarboxaldehyde¹¹. Short literature review below is devoted to the azines and their azomethine analogues investigated in this work. Lee et al.²⁵ described synthesis of azines via condensation of adduct 1:1 hydrazine and carbon dioxide with salicylaldehyde, benzaldehyde and others. Pomar et al.²⁶ used triisopropylsilylhydrazine for synthesis of various azines. Shah et al^{27} obtained azines via thermal transformation of aryl semicarbazones at 260°C. Also in papers²⁸⁻³⁰ different methods of azines synthesis were reported. Crystalline structure of salicylazine was investigated by Mijanuddin et al.³¹. Third – order nonlinear behavior of azines synthesized from thiophenaldehyde and its bromosubstituted derivatives were investigated by Ghazzali et al.³². Lin et al.³³ described crystalline

structures of thiophene and methylthiophenazines azines complexed with Fe₂(CO)₉. Crystalline structure of complexes of azines bearing pyridine moieties with different silver salts were investigated by Kennedy et al⁶ and by Vatsadze et al³⁴. Azines from triphenylaminoaldehyde and 4-(diethyamino)benzaldehyde were found by Fu et al³⁵ to be very effective for Hg²⁺ ion detection. One of the azines presented in our work, that is, the one prepared from salicylaldedyde and hydrazine, was investigated as AIEE compound¹⁰.

The main goal of this work is the comparison of properties of symmetrical azines with their azomethine analogues considering their structural (NMR, IR), thermal (DSC), optical (UV-vis, PL), and electrochemical (CV) properties and discussion in relation to the published literature data as well. Additionally, the electronic properties of obtained compounds are described theoretically by density functional theory (DFT).

2. Experimental part

2.1. Materials

4-(Diphenylamino)benzaldehyde, 4-pyridinecarboxaldehyde, 2-thiophenecarboxaldehyde, 2hydroxybenzaldehyde, hydrazine monohydrate (98%), trichloroacetic acid and *N*,*N*dimethylacetamide (DMA) were obtained from Aldrich. Ethanol (anhydrous), benzaldehyde and acetic acid (99.5%) were supplied from POCH and 1,4-phenylendiamine was obtained from Fluka. Azine AZ-4 and azomethine AZ-5 were described in our previous work¹⁹ and²⁰.

2.2. Synthesis of azines and azomethines

2.2.1. Synthesis of azines AZ-1 and AZ-3.

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Into aldehyde: benzaldehyde (1.0612 g, 10 mmol) or 4-pyridinecarboxaldehyde (1.0711 g, 10 mmol) dissolved in 5 ml ethanol the solution of hydrazine (0.2043g, 4 mmol) in 3 ml ethanol was added dropwise. After few seconds yellow product started to precipitate and 2 ml ethanol was added. The reaction mixture was stirred for 2 h at room temperature. The precipitate was filtrated, washed several times with ethanol and dried at 50°C in vacuum for 2 days. **AZ-1**: Yellow powder. Yield: (0.32 g) 48%. ¹H NMR (CDCl₃, δ , ppm): 8.67 (s, -CH=N, 2H), 7.85 (d, 4H), 7.45 (m, 6H). FTIR (cm⁻¹): 1624 (CH=N stretching), 3000 (CH aromatic). ¹³C NMR (CDCl₃), (ppm), δ : 162.05 (CH=N), 134.13, 131.21, 128.80. Elem. anal. calcd (%) for (C₁₄H₁₂N₂) (208.26): C 80.74, H 5.81, N 13.45; found C 80.90, H 6.08, N 13.28. DSC: I heating run (sample after synthesis, heating rate 20 °C/min) T_m 95 °C. cooling run (cooling rate 15 °C/min) crystallization (max exothermic peak) 72°C

II heating run (after rapid cooling and cooling rate 15 °C/min) $T_m\,96$ °C

 $T_m=95$ °C in ref.²⁷

AZ-3: Yellow powder. Yield: (0.76 g) 76%. ¹H NMR (CDCl₃, δ , ppm): 8.76 (d, 4H), 8.57 (s, -CH=N, 2H), 7.70 (d, 4H). ¹³C NMR (CDCl₃), (ppm), δ : 160.43 (CH=N), 150.58, 122.10. FTIR (cm⁻¹): 1628 (CH=N stretching), 3028 (CH aromatic). Elem. anal. calcd (%) for (C₁₂H₁₀N₄) (210.23): C 68.56 H 4.79 N 26.64; found C 68.66, H 4.88, N 26.82. DSC: I heating run (sample after synthesis, heating rate 20 °C/min) T_m 187 °C. cooling run (cooling rate 15 °C/min) crystallization (max exothermic peak) 164°C II heating run (after rapid cooling and cooling rate 15 °C/min) T_m 187 °C.

2.2.2. Synthesis of azine AZ-2.

Into salicylaldehyde (1.2212 g, 10 mmol) dissolved in 5 ml ethanol the solution of hydrazine (0.3037 g, 5 mmol) in 4 ml ethanol was added dropwise. The reaction mixture was stirred for

24 h at room temperature. The precipitate was filtrated, washed several times with ethanol and dried at 50°C in vacuum for 2 days.

AZ-2: Yellow powder. Yield: 75%. ¹H NMR (DMSO, δ, ppm): 11.12 (s, -OH, 2H), 9.01 (s, -CH=N, 2H), 7.70 (d, 2H), 7.40 (t, 2H), 6.98 (m, 4H). ¹³C NMR (CDCl₃), (ppm), δ: 162.78 (CH=N), 159.82, 133.44, 132.55, 119.72, 117.16. FTIR (cm⁻¹): 1624 (CH=N stretching), 3043 (CH aromatic).

DSC: I heating run (sample after synthesis, heating rate 20 °C/min) $T_m 220$ °C. cooling run (cooling rate 15 °C/min) crystallization (max exothermic peak) 156°C II heating run (after rapid cooling and cooling rate 15 °C/min) $T_m 220$ °C

 $T_m=216$ °C in ref.³⁶

2.2.3. Synthesis of azine AZ-5

4-(Diphenylamino)benzaldehyde (0.5467 g, 2 mmol) was dissolved in 10 ml ethanol at 60(C and then solution of 1 mmol of hydrazine (0.0511 g, 1 mmol) in 1 ml ethanol was added dropwise. The solution was heated to 80(C. After few minutes yellow product started to precipitate. The reaction mixture was stirred for 4 h at 80(C. The precipitate was filtrated, washed several times with ethanol (cold and hot) and dried at 50(C in vacuum for 1 day. AZ-5: Yellow powder. Yield: (0.44 g) 81%. 1H NMR (CDCl3, (, ppm): 8.57 (s, -CH=N, 2H), 7.65 (d, 4H), 7.29 (t, 8H), 7.14 (d, 8H), 7.08 (t, 4H), 7.05 (d, 4H). 13C NMR (CDCl3), (ppm), (: 160.88 (CH=N), 150.43, 147.00, 129.46, 125.39, 123.94, 122.70. FTIR (cm-1): 1616 (CH=N stretching), 3034 (CH aromatic). Elem. anal. calcd. (%) for (C38H30N4) (542.67): C 84.10, H 5.57, N 10.32; found C 83.01 H 5.72 N 10.09.

DSC: I heating run (sample after synthesis heating rate 20 °C/min) 242°C

cooling run (cooling rate 15 °C/min) crystallization (max exothermic peak) 207°C

II heating run (after rapid cooling and cooling rate 15 °C/min) T_g 77 °C, "cold" crystallization (max exothermic peak) 126, 197 T_m 242 °C

2.2.4. Synthesis of azomethine AM-1

Into 1,4-phenylendiamine (0.5405 g, 5 mmol) dissolved in 4 ml ethanol the solution of benzaldehyde (1.0612 g, 10 mmol) in 6 ml ethanol was added. The reaction mixture was stirred for 2 h at 80°C and cooled to room temperature. The precipitate was filtrated, washed several times with ethanol and dried at 50°C in vacuum for 2 days.

AM-1: Yellow powder. Yield: (0.86 g) 63%. ¹H NMR (CDCl₃, δ , ppm): 8.52 (s, -CH=N, 2H), 7.92 (dd, 4H), 7.49 (d, 6H), 7.29 (s, 4H). ¹³C NMR (CDCl₃), (ppm), δ : 159.79 (CH=N), 149.95, 136.22, 131.35, 128.78, 121.82. FTIR (cm⁻¹): 1615 (CH=N stretching), 3027 (CH aromatic). Elem. anal. calcd (%) for (C₂₀H₁₆N₂) (284.35): C 84.48, H 5.67, N 10.21; found C 85.16, H 5.86, N 9.89.

DSC: I heating run (sample after synthesis, heating rate 20 °C/min) T_m 142 °C. cooling run (cooling rate 15 °C/min) crystallization (max exothermic peak) 130°C II heating run (after rapid cooling and cooling rate 15 °C/min) T_m 142 °C

2.2.5. Synthesis of azomethine AM-2

Salicylaldehyde (0.2442 g, 2 mmol), 1,4-phenylendiamine (0.1081 g, 1 mmol) and a pinch of trichloroacetic acid were added to 5 ml DMA and heated (160°C) under argon atmosphere. After 17 h the mixture was cooled to room temperature. The precipitate was collected by filtration, washed with hot methanol and dried.

AM-2: Orange powder. Yield: (0.10g) 33%. ¹H NMR (DMSO, δ, ppm): 13.07 (s, -OH, 2H), 9.03 (s, -CH=N, 2H), 7.68 (d, 2H), 7.55 (s, 4H), 7.42 (t, 2H), 6.99 (m, 4H). ¹³C NMR (CDCl₃), (ppm), δ: 163.16 (CH=N), 161.18, 147.17, 133.30, 132.33, 122.26, 119.16, 117.31

FTIR (cm⁻¹): 1615 (CH=N stretching), 3053 (CH aromatic).

DSC: I heating run (sample after synthesis, heating rate 20 °C/min) $T_m 211$ °C. cooling run (cooling rate 15 °C/min) crystallization (max exothermic peak) 180°C II heating run (after rapid cooling and cooling rate 15 °C/min) $T_m 210$ °C

2.2.6. Synthesis of azomethine AM-3

Into 4-pyridinecarboxaldehyde (1.0711 g, 10 mmol) dissolved in 2.5 ml ethanol the solution of 1,4-phenylendiamine (0.5405 g, 5 mmol) in 5.5 ml ethanol was added. The reaction mixture was stirred for 2 h at 80°C, then cooled to room temperature and kept in the fridge overnight. The precipitate was filtrated, washed several times with ethanol and dried at 50°C in vacuum for 2 days.

AM-3: Yellow powder. Yield: (0.39 g) 30%. ¹H NMR (CDCl₃, δ, ppm): 8.77 (d, 4H), 8.52 (s, -CH=N, 2H), 7.77 (d, 4H), 7.34 (s, 4H). ¹³C NMR (CDCl₃), (ppm), δ: 157.64 (CH=N), 150.62, 149.66, 142.67, 122.15. FTIR (cm⁻¹): 1633 (CH=N stretching), 3031 (CH aromatic). Elem. anal. calcd (%) for (C₁₈H₁₄N₄) (286.33): C 75.50 H 4.93 N 19.57; found C 75.18, H 5.14, N 19.19.

DSC: I heating run (sample after synthesis, heating rate 20 °C/min) T_m 189 °C. cooling run (cooling rate 15 °C/min) crystallization (max exothermic peak) 147 °C II heating run (after rapid cooling and cooling rate 15 °C/min) T_m 188 °C

2.2.7. Synthesis of azomethine AM-4

Into 2-thiophenecarboxaldehyde (1.1215g, 10 mmol) dissolved in 3 ml ethanol the solution of 1,4-phenylendiamine (0,5407g, 5 mmol) in 7 ml ethanol was added dropwise and then 2 drops of acetic acid were added. The reaction mixture was stirred for 3 h at 80°C and the precipitate was filtrated, washed several times with ethanol and dried at 40°C in vacuum.

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AM-4: Yellow powder. Yield: (1.23 g) 84%. ¹H NMR (CDCl₃, δ , ppm): 8.61 (s, -CH=N, 2H,), 7.51 (d, 2H), 7.49 (d, 2H), 7.27 (s, 4H), 7.14 (t, 2H). ¹³C NMR (CDCl₃), (ppm), δ : 152.31 (CH=N), 149.30, 142.88, 132.12, 130.28, 127.74, 121.89. FTIR (cm⁻¹): 1608 (CH=N stretching), 3068 (CH aromatic). Elem. anal. calcd (%) for (C₁₆H₁₂N₂S₂) (296.41): C 65.28 H 3.42 N 9.51; found C 65.27, H 4.01, N 9.61.

DSC: I heating run (sample after synthesis, heating rate 20 °C/min) T_m 175 °C.

cooling run (cooling rate 15 °C/min) crystallization (max exothermic peak) 166°C

II heating run (after rapid cooling and cooling rate 15 °C/min) T_m 176 °C

 $T_m=150^{\circ}C$ in ref.³² and 148-149 °C in ref.³³

2.3. Blend preparation

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

2.4. Measurements

Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker AC 400 MHz spectrometer using chloroform-d (CDCl₃) or DMSO-d₆ as solvent and TMS as the internal standard. FTIR spectra were recorded on a BIO-RAD FTS 40 A Spectrometer using KBr pellets. 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. UV-vis absorption spectra were recorded using a Lambda Bio 40 Perkin Elmer spectrophotometer. The PL spectra were obtained on a VARIAN Cary Eclipse Fluorescence Spectrophotometer.

counting technique (Becker & Hickl, SPC-150). The samples were excited with 30 ps pulsed laser at λ_{ex} =405 nm with the repetition rate of 20 MHz. Fluorescence was filtered using FGL515 longpass filter combined with a band-pass filter 550/40 and detected with a fast avalanche photodiode (idQuantique id100-50). We measured 30 decays for different places across every sample. Electrochemical measurements were carried out using Jaissle IMP 83 PC T-BC potentiostat. Cyclic voltammetry experiments were conducted in a standard onecompartment cell, in dichloromethan (Fluka, HPLC grade). 0.1M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆ Aldrich, 99%) was used as the supporting electrolyte. The oxidation and reduction potentials of film coated on a ITO disk were measured using a Pt wire and a Ag/AgCl electrode as a counter electrode and a quasi reference electrode, respectively. Potentials were referenced with respect to ferrocene (Fc), which was used as the internal standard. The HOMO and LUMO levels were calculated by assuming the absolute energy level of Fc/Fc+ as -4.82 eV to vacuum. Theoretical DFT calculations were carried out using Gaussian09 package³⁷.

3. Results and discussion

In this article we describe our on-going efforts in the synthesis of materials for potential optoelectronic applications and the conjugated low molecular weight compounds bearing in structure imine linkages, that is, azines and their azomethine analogues.

3.1. Synthesis and characterization

The azines (abbreviated in text as AZ) and azomethines (abbreviated in text as AM) were prepared in a condensation reaction of various aldehydes such as: 4-diphenylaminobenzaldehyde, 4-pyridinecarboxaldehyde, 2-thiophenecarboxaldehyde, 2-

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hydroxybenzaldehyde and benzaldehyde and hydrazine and 1,4-phenylenediamine, respectively. The chemical structures of the obtained compounds are presented in Fig. 1.

[Fig.1.]

It should be noticed that the data concerning AZ-4 and AM-5 have been described in our previous works and here are repeated for comparison with AM-4 and AZ-5, respectively^{19,20}. Instrumental techniques including FTIR, ¹H NMR and ¹³C 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. The absence of the residual amino and aldehyde groups together with the appearance of a band typical for imine bonds was confirmed by NMR and FTIR spectra. The chemical shifts of the imine protons and carbons and IR absorption band of imine unit are presented in Table 1.

[Table 1]

In the ¹H NMR spectra of the investigated compounds the imine proton signal was observed in the range of 8.40–9.03 ppm. It can be seen that in the azines the signal of hydrogen in CH=N group in ¹H NMR spectra was shifted to lower field values in comparison with the azomethines synthesized from the same aldehydes. The biggest differences in the chemical shifts were observed in the compounds obtained from thiophene aldehyde **AZ-4** and **AM-4** (0.18 ppm) and from triphenylamine aldehyde **AZ-5** and **AM-5** (0.17 ppm) and **AZ-1** and **AM-1** (0.15 ppm). This seems to confirm the better conjugation in azines in comparison with their azomethine analogues. The only reverse behavior was detected in the compounds synthesized from –OH substituted aldehyde i.e. salicylaldehyde. However, in this case the difference in CH=N group proton signal in ¹H NMR was very small. Moreover, in these compounds, that is, **AZ-2** and **AM-2**, the signal of the CH=N group proton was significantly downfield shifted in comparison with the other AZ and AM investigated in this work. It indicates the highest degree of conjugation of π -electrons with phenyl ring π -electrons in both **AZ-2** and **AM-2** compared with other compounds probably due to better planarization as a consequence of possibility for intramolecular hydrogen bond formation between hydroxylic group and nitrogen³¹. In the ¹³C NMR spectra of the AZ and AM, the signals in the range of 152.31–163.16 ppm, present in the spectra of all compounds, confirmed the existence of carbon atoms in the imine group. Considering the signal of carbon in CH=N group in ¹³C NMR in relation to chemical structure of obtained compounds the same direction of the shift was found as for the signal of hydrogen atom in imine group in ¹H NMR. In FTIR spectra of investigated compounds the band characteristic for the HC=N- stretching vibration was detected in each case in the spectral range of 1608–1633 cm⁻¹ (cf. Table 1). From the literature data it follows that a free, isolated C=N group absorbs at about 1660 cm⁻¹ and this band is associated with the stretching vibrations of this group³⁸. The frequency of this band is strongly reduced with conjugation of the C=N group with phenyl ring due to diminishing of the energy of the C=N bond and delocalization of nitrogen pair into imine double bond.

The expected composition of the chosen investigated compounds was confirmed by elemental analysis as well. The results of the elemental analysis were compared with the calculated values of carbon, hydrogen, and nitrogen contents and show rather good agreement between calculated and experimentally determined values.

Differential scanning calorimetry (DSC) in nitrogen atmosphere was utilized to examine thermal properties of the obtained azomethines and azines. It is clear that thermal properties of the compounds depended strongly on their chemical structure and different behavior of imines and azines during DSC heating and cooling runs was observed. DSC thermogram of most azines and azomethines, that is, with phenyl (AZ-1, AM-1), hydroxyphenyl (AZ-2, AM-2), pyridine (AZ-3, AM-3) and thiophene units (AZ-4, AM-4) during first heating run (heating rate 20 °C/min) showed one endotherm indicating melting of

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the sample. During cooling (at heating rate 15 °C/min and rapid cooling) only one exothermic peak in DSC thermograms was observed confirming crystallization of the compounds. The second heating scan revealed only the melting point. A different behavior was found in the case of the azine and azomethine containing the TPA moiety (AZ-5 and AM-5). DSC thermograms of AZ-5 are presented in Fig. 2.

[Fig.2]

The DSC thermogram of AZ-5 features endothermic peak confirming melting of the sample at 242°C during first heating run. After rapid cooling, during second heating run, glass transition at 77°C, "cold" crystallization (exothermic peak) at 126 and 197°C, and melting endotherm at 242 °C were detected. The observed double cold-crystallization exotherms in samples of low crystallinity could be attrbited to three various phenomena: (i) to the superposition of the melting of crystals, formed by the annealing pretreatments, and the coldcrystallizations occurring during DSC heating³⁹, (ii) the competition between the crystallization from the nuclei formed during cooling, and that from spontaneous nucleation⁴⁰ and (iii) co-existence of two kinds of amorphous regions⁴¹. In the case of AM-3 during first heating run "cold" crystallization at 145 °C, and melting point at 195°C was found, as reported in our previous work²⁰. On the other hand, after rapid cooling, the second heating scan revealed only glass transition at 83 °C. Thus, AZ-5 and AM-5 exhibit behavior typical for molecular glasses consisting of melting temperature (T_m) of the crystalline sample and when isotropic liquid was cooled down, a glass was spontaneously formed via a supercooled liquid. Next, when the amorphous glass sample was again heated, a glass-transition phenomenon was observed and on further heating above T_g , the T_m could be detected^{18,42}. Molecular glasses may form uniform, transparent amorphous thin films by vapor deposition and spin-coating methods contrary to low molar mass compounds with strong tendency for crystallization. Films from crystalline materials could be prepared only by using polymeric binders. Azines prepared from the same aldehydes as azomethines exhibited comparable values of T_m as expected for AZ-1 and AM-1.

3.2. Optical properties

The optical properties of the obtained compounds were analyzed by UV-vis and PL spectroscopies. The solvatochromic behavior of the azines and azomethines in various solvents (chloroform, THF, NMP, DMSO) with different dipole moments and consequently with a different polarity was studied. Optical properties of the compound in the solid state as a blend with nonemissive poly(methyl methacrylate) (PMMA) were investigated as well. Dispersed luminescent compound in nonemissive polymer matrix provide a way to eliminate the self-quenching of fluorescence due to the dilution effect^{43,44}. Polymer blends involving luminescent compound and inert polymers as matrices are often used in polymer light emitting diodes as a tool to increase the efficiency of the devices^{43,45}. Additionally, the UV-vis and PL properties of the compounds before and after protonation with HCl were tested.

3.2.1. Ultraviolet-Visible Investigations

The spectroscopic data and exemplary UV-vis spectra of investigated compounds are presented in Table 1S in Supporting Information and Fig. 3, respectively.

[Fig.3]

In most cases absorption spectra of azines and azomethines showed similar characteristics in all solvents, that is, they exhibit two absorption bands, one in lower energy region with maximum (λ_{max}) in the range of 270-297 nm, and second with λ_{max} located between 355 and 407 nm. Two azines containing phthalic and pyridine rings (AZ-1 and AZ-3) exhibited one absorption band with λ_{max} around 300 nm (cf. Fig. 2a). Taking into account the UV-vis spectral data it was found that the λ_{max} position shows no clear dependence on the dielectric constant of the solvent. Absorption bands in CHCl₃ (ϵ =4.81) and DMSO (ϵ =46.70) were

hypsochromically or batochromically shifted in the range of 7 nm, depending on the compound structure. Fig. 3c, d displays the influence of the solvents on absorption bands of **AZ-1** – **AM-1** and **AZ-3**. The influence of the dielectric constant of the solvent on molar absorption coefficient was more pronounced (cf. Fig. 3e and Table 1S). Absorption bands at the longest wavelength were found for the compounds with triphenylamine units i.e. **AZ-5** and **AM-5**. The compounds from salicylaldehyde **AZ-2** and **AM-2** absorbed the light at about 50 nm shorter wavelengths. The azomethines absorbed at longer wavelengths in comparison with the azines synthesized from the same aldehydes, except the ones with triphenylamine moieties.

The influence of protonation on absorption properties in UV-vis range was also investigated. From theoretical point of view protonation of nitrogen atom in CH=N unit should lead to bathochromic shift of UV-vis absorption band because involving free electron pair of nitrogen atom with hydrogen bonding formation enables twist of aldehyde aromatic ring, which enhances conjugation of π electrons of CH=N and aromatic ring. In this study the azines and azomethines were protonated with HCl in NMP solution using equimolar amount of HCl and CH=N group and the results are presented in Table 2. We find that only pairs AZ-1 - AM-1, AZ-3 - AM-3 and AZ-4 - AM-4 follow the theoretical prediction, in these cases protonation causes bathochromic shift of electronic absorption bands and the differences in absorption wavelengths of protonated and unprotonated samples were in the range of 6-37 nm. For other compounds hypsochromic shift of the absorption band after protonation was observed; the biggest effect, amounting to a 64 nm shift, was found for AZ-5 and AM-2. Azines with phenylene (AZ-1) and pyridine (AZ-3) moieties exhibited higher bathochromic shift of absorption bands than the azomethine analogues (AZ-1 and AZ-3). It is necessary to point out that in AZ-3 and AM-3 there are four nitrogen atoms, which can be protonated i.e. in CH=N groups and in the pyridine rings. Therefore, the electronic spectra were detected in NMP using 2 moles and 4 moles of HCl on 1 mole of the compound as well. When the ratio of **AZ-3** or **AM-3** to HCl was 1:4, the value of λ_{max} was found at the same wavelength. Thus, along with increasing the amount of protonation agent shows no effect on the λ_{max} . In the case of these compounds, probably, mainly interaction of HCl with nitrogen present in pyridine ring takes place. Similar as it was observed in compounds with imine linkages prepared from 3,8-diamino-6-phenylphenanthridine in which mainly nitrogen in phenanthridine structure was protonated^{46,47}.

Electronic spectra were also detected for blends of the azines and azomethimes in polymethylmethacrylate (PMMA). In most cases absorption bands in solid state were bathochromically shifted in comparison with respective solutions.

3.2.2. Photoluminescence

Emission spectra of the azines and azomethines were investigated in CHCl₃, THF, NMP and DMSO and in solid state and using various excitation wavelengths (λ_{ex}). The corresponding data is collected in Table 2S in Supporting Information. It was found that both the choice of the solvents and the excitation wavelength influenced the emission spectrum and also its intensity. Three of the investigated compounds (without AZ-4 and AM-5), that is, AZ-2, AM-2 and AZ-5 emitted light in all considered solvents. In chloroform solution, the emission of azines and azomethines with phenyl (AZ-1, AM-1), pyridine (AMZ-3, AM-3) and imine with thiophene (AM-4) rings was very week. Moreover, AZ-1, AZ-3, AM-3, and AM-4 practically exhibit no emission in DMSO solution. It was observed that heteroatomic azomethine with thiophene units (AM-4) exhibited photoluminescence only in NMP solution. As an example, Fig. 4a. shows influence of the solvent on photoluminescence spectra for AZ-5 under λ_{ex} =340 nm excitation, whereas Fig.1S in Supporting Information presents

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photographs of the compounds in CHCl₃, NMP solution, and in blends irradiated with 366 nm light .

[Fig.4]

As it can be seen in Fig. 4, the choice of the solvent influences not only the intensity and maximum of emission wavelength (λ_{em}), but also the spectrum shape. The observed broadening of the emission spectrum can be explained as a result of increase of conformational disorder⁴⁸. It was found that photoluminescence intensity depended also on the excitation wavelength. As an example, the relationship between photoluminescence intensities and λ_{em} and excitation wavelengths in chloroform solution are illustrated in Fig. 4b. for AZ-5. For all the compounds an increase of excitation wavelength caused a shift of emission band towards lower energies. However, in the most cases, the maximum emission band with the highest intensity in different solvents was observed at different excitation wavelengths (cf. Table 2S). It is obvious that the compound structure plays important role in determining the PL properties. Fig. 4c presents λ_{em} of investigated compounds in NMP solution under the same λ_{ex} equal to 360 nm. When considering the photoluminescence in NMP solvent, it was found that for the azines, with the exception of AZ-2, the maximum emission was observed under excitation at 330-350 nm, while for the azometines the highest intensity was observed under excitation at 420-450 nm. The azomethines emitted light with maximum intensity at longer wavelengths than the azines, the maximum emission ranges from 517 nm (AM-4) to 497 nm (AM-3) in NMP solution. For azines in the same solvent, the λ_{em} position was hypsochromically shifted and appears between 477 nm (AZ-5) and 400 nm (AZ-3). The compounds synthesized from salicylaldehyde exhibited the reverse behavior. In this case, the azine AZ-2 emitted light with the highest intensity at longer wavelength (539 nm), while AM-2 emission was hypsochromically shifted to 403 nm. Bathochromic shift of the λ_{em} in NMP of azomethine and azine was detected for the pair AM-4 - AZ-4 being equal

to 111 nm, for AM-3 – MZ-3 : 97 nm, and for AM-1-AZ-1 : 82 nm. For the pair AM-2 – AZ-2 the maximum emission band for the azomethine was hypsochromically shifted by 136 nm in comparison with the azine. It was found that azomethine with thiophene rings (AM-4) exhibited emission with the lowest intensity. The AM-1 and AM-4 described in literature emitted light with λ_{em} at 410 and 416 nm in acetonitrile, respectively.

Additionally, in investigations of optical properties, the Stokes shifts estimated as a difference between the 0–0 peaks of absorption and PL spectra, were analyzed. From a practical point of view, large Stokes shifts are desirable in order to avoid self-absorption of emitted light that reduce luminescence efficiency in devices⁴⁹. The calculated Stokes shift values of the studied compounds are collected in Table 4.

[Table 4]

The Stokes shift was calculated for the most intense emission band in given solution. The highest value of Stokes shift was observed for azine with pyridine rings (AZ-3).

Next step of PL characterization of azines and azomethines concerns their emission properties in solid state as a blend with PMMA. PL spectra of blends were recorded under λ_{ex} which gave the highest emission in NMP solution. Remarkably, we find that significant differences in photoluminescence of the azines and the azomethimes in NMP solution (considering position of λ_{em} with the highest intensity) were less pronounced in blends of the compounds with PMMA. Even though the azomethines in blend emitted at longer wavelengths (except for AM-2) than the azines, the shift of the bands was in the range of 16-85 nm, while in the case NMP solution was in the range of 73-136 nm. In the case of the compounds from salicylaldehyde, the emission band of **AZ-2** was bathochromically shifted by 57 nm in comparison with that of **AM-2**, i.e. the reversed behavior was found than in the other pairs. However, all compounds in blends with PMMA emitted blue light (cf. Fig. 4c). It should be mentioned that emission of **AZ-5** blend was not registered because of too high PL Page 19 of 47

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intensity. The position of the emission band of blends was bathochromically shifted in relation to the compound in NMP solution except for AZ-4 and AM-4 (cf. Fig.5a).

[Fig. 5]

As it was mentioned, the presence of nitrogen atom, that is, the atom with a free electron pair, in imine units, gives an opportunity for modification of the optical properties due to protonation with HCl. Protonation of the compounds was carried out at room temperature in NMP solution. Fig. 5b shows the influence of protonation with HCl on photoluminescence intensity for AZ-1. In most cases, upon protonation, we observed an increase of photoluminescence intensity, except for the AZ-5 where protonation resulted in reduced PL intensity and hypsochromical shift of the emission band by 27 nm.

Additionally, photoluminescence lifetime measurements were performed on blends of synthesized azines (AZ1-AZ-3, AZ-5) and azomethines (AM-1-AM-4) under λ_{ex} =405 nm. In Fig. 6 we show examples of the measured fluorescence transients obtained for the pair AZ-2 and AM-2.

[Fig. 6]

Red points correspond to transients fitted with three-exponential decay characteristics, while transients displayed in blue were obtained for the same sample but at different places across it. The first observation derived from the time-resolved experiments concerns the uniformity of the blends. In all cases the distribution and variation of measured transients were minimal, resulting in decay time changes less than 10%. Such a small variation indicates excellent uniformity of the structure and homogeneous molecular ordering in the blends. These observations are important for applying these materials as possible light emitting devices. In order to quantitatively analyze measured transients, we approximated them with three-exponential decay model, with the exception of **AM-4**, where two-exponential model yielded high-quality fit. Obtained decay constants are summarized in Table 5.

[Table 5]

The fastest decays are obtained for AZ-2 and AM-2 pair of all the studied molecules, while AZ-3 and AM-3 pair exhibit the longest transient behavior. In the first case the longest decay constants are lower than 5 ns, while in all other samples they are around 7 ns. From the results included in Table 5 it is also apparent that in general the decay constants determined for azines are shorter than those obtained for azomethimes.

3.3. DFT calculations

We performed the quantum theoretical calculations using density functional theory (DFT), with an exchange correlation hybrid functional B3LYP and the basis 6-31G(2d,p) for carbon, nitrogen, oxygen, 6-311G(3d,p) for sulfur and 6-31G for hydrogen atoms. The simulated geometries of these compounds were optimized in vacuum and no imaginary frequencies were found for any of these species, computed at C_i symmetry, by vibrational analysis. Moreover, comparison of calculated and experimentally measured IR spectra show good agreement; the differences between calculated and experimental CH=N stretching band is less than 25 cm⁻¹ (cf. Table1). Exemplary calculated and experimental IR spectra of AZ-2 and AM-2 are shown in Supporting Information, Fig. 1S. Based on the optimized geometries, the energy and electronic distribution of molecular frontier orbitals were calculated in acetonitrile. The solvent effect was introduced by PCM model. The frontier orbitals are of extreme importance for the evaluation of molecular reactivity. is the higher is the negative the energy of the Highest Occupied Molecular Orbital (HOMO), the more susceptible is the molecule to donate electrons and, consequently, higher is the tendency to suffer oxidation. A similar argument can be used to interpret the tendency of a given molecule to suffer reduction, on the basis of the energy of the Lowest Unoccupied Molecular Orbital (LUMO). The contours of HOMOs and LUMOs of exemplary compounds (AZ-1, AM-1, AZ-3, AM-3, AZ-

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5 and **AM-5**) are depicted in Fig.7, whereas data obtained for **AZ-2**, **AM-2**, **AZ-4** and **AM-4** are included in Supporting Information, Fig. 2S.

[Fig. 7]

In general, for all these molecules, the HOMO orbitals were concentrated in the aromatic rings and in its neighborhood (-CH=N-), indicating that the oxidation process should happen primarily in this region. This corresponds to the calculations of electronic density, which indicate that this region has the highest density of negative charge (cf. Fig. 8).

[Fig. 8]

LUMOs are localized on nonbonding p_z orbitals excluding double bonds and aromatic parts of the molecules. The calculated frontier orbital energy levels are shown in Table 5.

[Table 5]

The calculated HOMO and LUMO levels of **AM-5** were -5.35 and -2.19 eV, respectively. Taking into account the character of molecular orbitals, we can draw several conclusions. The HOMOs energies of azine compounds (**AZ**) are lower than azomethine ones (**AM**). This can be explained by the fact that a phenyl group is incorporated between =N-N= group and expected π - π conjugation effect leads to a rise in HOMO energy. Moreover, the oxidation process involves the removal of an electron from HOMO, thus azomethine compounds with higher energy levels would be more susceptible to donate electrons.

The calculation results indicated that the introduction of a hydroxyl substituent to the phenyl ring decreased the HOMO energy (**AM-1** vs **AM-2**), which is consistent with the experimental data. Similarly, replacement of phenyl ring in **AM-1** compound by pyridine or thiophene results in a decrease of the HOMO energy.

3.4. Electrochemical properties

Cyclic pulse voltammetry (CV) is a useful and valuable technique to study redox behavior, electrochemical stability, and to get information about HOMO and LUMO energy values of hole and electron transport materials and to examine the barriers for charge injection. The electrochemical behavior of the azines (AZ-1-AZ-3, and AZ-5) and azomethines (AM-1-AM-4) was studied by CV for samples deposited as films on ITO substrates. All tested compounds exhibited electrochemical behavior. The obtained electrochemical data are listed in Table 6 and the exemplary cyclic voltammograms of AM-4 are shown in Fig. 9.

All of the azines demonstrated only irreversible one or two step reduction processes (except for **AZ-4** and **AZ-5**), whereas the azomethines showed both oxidation and reduction process, however, also irreversible. For **AZ-4** the reduction was a quasi-reversible in nature and this azine also exhibited irreversible oxidation¹⁹. The HOMO and LUMO energy levels of the compounds were estimated from the electrochemical oxidation and reduction onset potentials, assuming the ionization potential (IP) of ferrocene to be equal to -4.8 eV, according to well-established equations⁵⁰

$$E_{HOMO} = -4.8 - E_{ox}(onset)$$

 $E_{LUMO} = -4.8 - E_{red}(onset)$

In the case when no reduction was observed, the LUMO level was estimated from the HOMO energy level and the onset of absorption (UV-vis) taking into account the optical band gap (E_g^{opt}) using the equation

$$E_{LUMO} = E_{HOMO} + E_g^{opt}$$

The LUMO level estimated by this method is not an accurate way of measuring the electron affinity, however, allows for selection of suitable combinations with electron acceptors in devices⁵¹.

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The lowest oxidation potentials (0.23 and 0.26 V vs. Fc (peak onset)) were recorded for AM-2 and AM-3, respectively (cf. Table 6). Considering the Eox (onset) it can be observed that the imines with hydroxyphenyl (AM-2) and pyridine (AM-3) rings were more readily oxidized than azomethine with phenyl (AM-1) and thiophene (AM-4) units. Comparing the ability for oxidation of azine (AZ-4) and their azomethine analogue (AM-4), it was found that azomethine was easier to oxidize. Taking into account the chemical structure of azines and their ability for reduction, it was observed that azines with pyridine (AZ-3) and thiophene (AZ-4) units were easier to reduce than azines with phenyl (AZ-1) and hydroxyphenyl (AZ-2). HOMO energy level of azines was in the range of -5.05- -5.59 eV. Azine AZ-4 exhibited significantly lower value of the HOMO energy level $(-6.12 \text{ eV})^{19}$ than its azomethine analogue (AM-4) (-5.59 eV). Azines with phenyl (AZ-1) and hydroxyphenyl (AZ-2) units showed lower value of LUMO level than their imine analogues (AM-1 and AM-2) contrary to AZ-3 and AZ-4, for which LUMO values were higher than azomethines with pyridine (AM-3) and thiophene rings. The HOMO and LUMO levels of AM-4, estimated based on CV measurements, correspond to the previously published data¹¹. Comparing the energy gap (E_{σ}) values of azines and azomethines obtained using both electrochemical and optical methods it can be concluded that imines are more conjugated than their azine analogue. The theoretically predicted HOMO energies are in good agreement with experimental data in the case of AZ-5, AM-5 and AM-1 compounds and much higher for AM-2 and AM-3. On the other hand, in all cases the DFT calculated LUMO levels are compatible with the CV data, except for AM-1. Generally, the theoretically estimated LUMO energy levels are lower than obtained from CV measurements (except for AZ-4). The differences may be related to various effects of conformations of compounds in films and in solvents, particularly that the calculated and experimental IR spectra correspond to each other (cf. Table 1).

4. Conclusions

Symmetrical azines and their azomethine analogues containing in their structure phenyl, hydroxyphenyl, TPA, and heteroatomic rings such as pyridine and thiophene were synthesized and characterized. The study revealed clearly pronounced effects of chemical structure on the optical and redox properties of both types of investigated compounds. The conclusions drawn from the study are as follows:

- azine and azomethine with TPA units form molecular glasses and show a glass transition at 77 and 83°C, respectively. Azines prepared from the same aldehydes as azomethines exhibited comparable values of melting point expect for compounds with phenyl rings. In this case higher T_m was observed for azomethine;
- UV-vis absorption band responsible for imine structure in the case of the azines was hypsochromically shifted in relation to azomethines obtained from the same aldehydes;
- all compounds emitted blue light in NMP solution and blended with PMMA. Heteroatomic imine with thiophene moieties emitted light only in NMP solution and with the lowest intensity as compared to the other compounds. Compounds with TPA units exhibited the highest PL intensity. Comparing PL properties of azines and their azomethine analogues it can be concluded that azomethines emitted light with the highest intensity with λ_{em} bathochromically shifted in relation to λ_{em} of azines (except for the compounds with hydroxyphenyl structure). The longest photoluminescence lifetime in blend was detected for compounds with pyridine ring, that is, AZ-3 and AM-3 pair. The blends reveal very good uniformity as measured using time-resolved fluorescence. In most cases, the protonation with HCl causes significant increase of PL intensity;

• electrochemical studies revealed that azines undergo irreversible reduction process, whereas, their azomethine analogues exhibit also the ability to oxidation, however, irreversible in nature. In the case of azine with thiophene units, both reduction and oxidation processes were observed. The presence of hydroxyphenyl and pyridine units in azomethines leads to higher HOMO levels. On the other hand, the value of LUMO level of these imines is lower than for other azomethines, which results in decreasing electrochemical energy gap. The investigated azines exhibit optical energy gaps in the range of 3.14–3.78 eV, therefore larger than corresponding azomethines (E_g = 2.72 – 3.02eV). Electrochemically evaluated E_g^{CV} was lower than E_g^{opt} and was in the range of 2.09 – 2.47 eV.

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Supporting Information Available

This information is available free of charge via the Internet at http://pubs.acs.org.

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- Fig. 1. Chemical structure of investigated compounds.
- Fig. 2. DSC scans of azine **AZ-5**: (a) I-run, heating at 20 °C/min and (b) II-run, heating at 20 °C/min after rapid cooling.
- Fig. 3. UV-vis absorption spectra of (a) azines, (b) azomethines in NMP (solution concentration was 1×10^{-5} mol/l), (c) azine AZ-1 and (d) azomethine AM-1 in various solvents (solution concentration was 1×10^{-5} mol/l). (e) The influence of solvents on molar absorption coefficient (ϵ) of AZ-3.
- Fig. 4. The emission spectra of AZ-5 (c = 1×10^{-4} M) (a) in various solvents under λ_{ex} = 340 nm, (b) under various excitation wavelength in NMP solution. (c) The maximum of emission wavelength (λ_{em}) of obtained compounds in NMP solution under λ_{ex} = 360 nm.
- Fig. 5. (a) The emission spectra in NMP solution in and blend with PMMA of AZ-3 under $\lambda_{ex} = 340$ nm and (b) the PL spectra of AZ-1 in NMP solution (c = 1 × 10⁻⁴ M) pristine and after doping with HCl under $\lambda_{ex} = 350$ nm.
- Fig.6. Fluorescence transients measured for AZ-2 and AM-2 blends excited with 405 nm pulsed laser. Red points are data fitted with solid black line, representing three-exponential decay behavior. Blue transients were measured for other places across the samples.
- Fig. 7. HOMO and LUMO contours of the obtained azines AZ-1, AZ-3, AZ-5 and corresponding azomethines AM-1, AM-3, AM-5.
- Fig. 8. Electrostatic potential on the AM-1, AZ-4, and AM-4 molecules.
- Fig. 9. Cyclic voltammograms of AM-4.











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Fig. 7.

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 Table 1. Chemical shift of the imine proton in ¹H NMR, imine carbon atom in ¹³C NMR spectra and imine absorption band in FTIR spectra of the investigated compounds.

Code	-CH=N-		
	¹ H NMR [ppm]	¹³ C NMR [ppm]	FTIR [cm ⁻¹]
AZ-1	8.67	162.05	1624 ^a 1641 ^b
AM-1	8.52	159.79	1615 ^a 1615 ^b
AZ-2	9.01	162.78	1624 ^a 1627 ^b
AM-2	9.03	163.16	1615 ^a 1628 ^b
AZ-3	8.57	160.43	1628 ^a 1641 ^b
AM-3	8.51	157.64	1633 ^a 1619 ^b
AZ-4	8.78	155.91	1608 ^a 1584 ^b
AM-4	8.60	152.31	1608 ^a 1614 ^b
AZ-5	8.57	160.88	1616 ^a 1628 ^b
AM-5	8.40	158.77	1622 ^a 1634 ^b
^a found, ^b	calculated		

Table 2. The Stokes shifts values considering the most intensive emission band in each

medium

Madium	Stokes shifts [cm ⁻¹]								
Medium	AZ-1	AM-1	AZ-2	AM-2	AZ-3	AM-3	AM-4	AZ-5	
CHCl ₃	-	-	9618	8859	-	-	-	5001	
THF	9859	-	-	8577	12890	-	-	4148	
DMSO	-	4166	11046	574	-	-	-	5680	
NMP	8493	7682	9537	1364	10971	6483	7539	3727	
NMP+HCl	6620	5051	6938	6816	10999	5991	-	7103	
blend	4137	4067	3528	1746	3920	5998	-	-	

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Table 3. Fluorescence decay times obtained by fitting multiexponential decay to

experime	ntally measured	l curves foi	blends.
Code	τ_1 [ns]	$\tau_2 [ns]$	τ ₃ [ns]
AZ-1	0.56	2.22	7.12
AZ-2	0.26	1.13	4.77
AZ-3	1.03	2.53	7.57
AZ-5	0.64	2.41	6.88
AM-1	0.42	2.96	7.38
AM-2	0.33	1.19	4.94
AM-3	0.64	2.58	7.86
AM-4	1.1	4.41	_

Code	AZ-1	AZ-2	AZ-3	AZ-4	AZ-5	AM-1	AM-2	AM-3	AM-4
E _{ox1} [V]	-	-	-	-	0.55	0.80	0,44	0.44	1.02
E _{ox2} [V]	-	-	-	-	0.71	1.44	1.00	1.42	1.30
E _{red1} [V]	-2.57	-2.26	-2.10	-	-	-2.07	-2.14	-2.02	-2.27
E _{red2} [V]	-	-	-2.60	-	-	-	-	-2.37	-
E _{ox} (onset) [V]	-	-	-	1.32 ¹⁹	0.42	0.70	0.23	0.26	0,77
E _{red} (onset) [V]	-2.22	-2.03	-1.74	- 1.78 ¹⁹	-	-1.75	-1.94	-1.81	-2.09
Е _{номо} (CV) [eV]	-	-	-	-6.12 ¹⁹	-5.26	-5,52	-5,05	-5,08	-5,59
E _{HOMO} (DFT) [eV]	-6.57	-6.24	-7.12	-6.07 -5.63 ¹⁹	-5.30	-5.79	-5.95	-5.94	-5.83
E _{LUMO} (CV) [eV]	-2,58	-2,77	-3,06	-3.02 ¹⁹	-	-3,05	-2,86	-2,99	-2,71
E _{LUMO} (DFT) [eV]	-2.34	-2.47	-2.90	-2.04 ¹⁹ -2.45	-1.22	-1.95	-2.34	-2.20	-2.50
E_{g}^{CV} [eV]	-	-	-	3.10 ¹⁹	-	2,47	2,19	2,09	2,88
Eg DFT [eV]	3.63	3.14	4.22	3.50 ¹⁹ 3.62	4.08	3.84	3.61	3.74	3.33
Eg ^{opt} [eV]	3.63	3.14	3.78	3.15	2.72	3.02	2.84	2.98	2.86
$E_g^{CV} = E_{ox}(onset) - E_{red}(onset) = E_{HOMO} - E_{LUMO}$									

Table 4. Experimental and calculated electrochemical data of investigated azines and imines



