

Phenoxazine Based Units- Synthesis, Photophysics and Electrochemistry

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Abstract A few new phenoxazine-based conjugated monomers were synthesized, characterized, and successfully used as semiconducting materials. The phenoxazine-based oligomers have low ionization potentials or high-lying HOMO levels (~ 4.7 eV), which were estimated from cyclic voltammetry. Conjugated oligomers offer good film-forming, mechanical and optical properties connected with their wide application. These results demonstrate that phenoxazine-based conjugated mers are a promising type of semiconducting and luminescent structures able to be used as thin films in organic electronics.

Keywords Phenoxazines · Stille condensation · Cyclic voltammetry · Conductivity · Luminescence · Atomic Force Microscopy (AFM)

Introduction

Conjugated organic semiconductors that have high charge carrier mobilities, solution process ability, and air stability are of enormous interest for applications in organic electronics, particularly thin film transistors [1–3], photovoltaic cells [4–7], electrochromic materials [8, 9], and light-emitting devices [10].

Phenoxazines usually have high luminescence quantum yields and are known as efficient laser dyes, are also

scarcely explored as building blocks in current OLED materials [11]. Several 1,4-benzoxazino[2,3-b]phenoxazines have been prepared and used as hole-injection materials in emitting materials [12]. Conjugated copolymers built of derivatives of phenoxazine and dialkylfluorene are well-known as semiconducting field effect transistors as well as electroluminescent tools [13, 14]. Despite the fact, compared to carbazoles, phenothiazines [15, 16], phenoxazine has attracted even much less attention as a building block in organic semiconductors [14]. However, phenoxazine-based donor-acceptor molecules have not yet been studied frequently. Furthermore, the chemical structure of phenoxazine resembles that of triphenylamine, which is widely used as a hole-transporting organic material. Thus, polymers/oligomers containing a phenoxazine unit could be promising conducting and fluorescent materials [17, 18].

The reason for this scarcity of polymer semiconductors for developing novel systems for electronic and optoelectronic devices is that the materials must meet many requirements. Most notably good π -electron delocalization along the chain and a high degree of intermolecular order, good intermolecular π -stacking and ordered supramolecular morphology, and sufficiently low ionization potential (IP) is demanded.

In this paper, continuing our concerns connected with electrochemistry of heterocyclic block structures [19], we report a previous study exploring the fused tricyclic phenoxazine ring as a building block for the construction of semiconducting and luminescent materials for electronic devices. A few new phenoxazine-containing π -conjugated mers, with the structure shown in Fig. 1, were synthesized and investigated.

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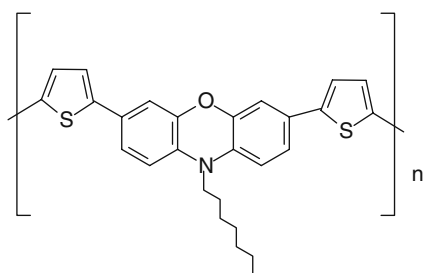


Fig. 1 Structure of poly [*N*-alkyl-bis(2-thiophene)phenoxazine]

Experimental

Materials and instruments

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded using a Bruker 300 spectrometer. Chemical shifts are denoted (internal TMS=0.0 ppm). Preparative column chromatography (CC) was carried out on glass columns of different sizes packed with silica gel Merck 60 (40–63 μm). MS spectra were taken on a Bruker micrOTOF-Q, FWHM-17500, 20 Hz. Phenoxazine, 1-bromobutane, 1-bromononane, 1-bromohexadecane, sodium hydride (60% in mineral oil), 2-(tributylstannyl)thiophene and 2-(tributylstannyl)furane were obtained from Aldrich and use as received. Tetrakis(triphenyl)phosphine palladium and 2-(tributylstannyl)pyridine were obtained from Lancaster and used as received. Anhydrous THF was purified by vacuum distillation before use.

Syntheses

3,7-Dibromo-*N*-alkylphenoxazine (**1b-c**)

3,7-Dibromo-*N*-alkylphenoxazines was synthesized according modified earlier procedures [13, 20–23] typical for alkylation's reactions.

*Selected data for 3,7-dibromo-*N*-hexadecylphenoxazine 1c* Y=41% (2.07 g), greenish crystals, mp. 65–66°C, $^1\text{H NMR}$ (CDCl_3) δ : 6.86 (dd, $J=2.21$ Hz, $J=2.21$ Hz, 2H, arom. H), 6.70 (d, $J=2.18$ Hz, 2H, arom. H), 6.26 (s, 2H, arom. H), 3.41–3.36 (m, 2H, CH_2), 1.57–1.54 (m, 2H, CH_2), 1.34–1.15 (m, 26H, CH_2), 0.87 (t, $J=6.62$ Hz, 3H, CH_3). $^{13}\text{C NMR}$ (CDCl_3) δ : 145.15, 132.13, 126.49, 118.51, 112.35, 112.14, 44.22, 34.02, 32.83, 31.91, 29.65, 29.54, 29.42, 29.34, 28.76, 28.16, 26.80, 24.63, 22.67, 14.11. Anal. Calc. for $\text{C}_{28}\text{H}_{39}\text{Br}_2\text{NO}$: C, 59.49; H, 6.91; Br, 28.29; N, 2.48; O, 2.83. FTMS-ESI (m/z): [M^+] calc. for $\text{C}_{28}\text{H}_{39}\text{Br}_2\text{NO}$, 565.01.

3,7-Bis(2-thiophene)-*N*-alkylphenoxazine (**2a-c**)

3,7-Bis(2-thiophene)-*N*-alkylphenoxazine (**2a-c**) Monomer (**2**) was synthesized according to our previous experience [22, 23] by a coupling reaction of 3,7-dibromo-*N*-alkylphenoxazine **1** (3.53 mmole) with 2-(tributylstannyl)thiophene (8.11 mmole), and tetrakis(triphenylphosphine)palladium (0) (0.40 mmol) as catalyst. The mixture was stirred at 100°C for 72 h under nitrogen. The reaction was then quenched by addition of 40 ml of water, than the water solution was extracted with chloroform. Organic phase was washed with water, dried, and the solvent was removed by rotary evaporator. The crude product was purified by column chromatography (hexane: ethyl acetate, 1:1).

*Selected data for 3,7-bis(2-thiophene)-*N*-butylphenoxazine 2a* Y=50% (0.2 g), yellowish oil, $^1\text{H NMR}$ (CDCl_3) δ : 7.69–7.63 (m, 2H, arom. H), 7.46 (d, $J=7.56$ Hz, 2H, arom. H), 7.16 (d, $J=4.17$ Hz, 2H, arom. H), 7.00 (d, $J=3.54$ Hz, 2H, arom. H), 6.78 (d, $J=5.34$ Hz, 2H, arom. H), 6.48 (s, 2H, arom. H), 3.52–3.46 (m, 2H, CH_2), 1.65–1.55 (m, 2H, CH_2), 1.46–1.33 (m, 2H, CH_2), 0.96 (t, $J=7.28$ Hz, 3H, CH_3). $^{13}\text{C NMR}$ (CDCl_3) δ : 144.85, 143.28, 132.90, 132.12, 131.99, 131.48, 129.08, 128.97, 128.58, 128.42, 127.90, 123.90, 122.06, 121.25, 118.23, 118.06, 112.94, 111.92, 111.21, 111.01, 43.87, 30.15, 20.08, 13.83. Anal. Calc. for $\text{C}_{24}\text{H}_{21}\text{NOS}_2$: C, 72.18; H, 5.26; N, 3.51; O, 3.01; S, 16.04. FTMS-ESI (m/z): [M^+] calc. for $\text{C}_{24}\text{H}_{21}\text{NOS}_2$, 399.21.

*Selected data for 3,7-bis(2-thiophene)-*N*-nonylphenoxazine 2b* Y=55% (0.22 g), yellow oil, $^1\text{H NMR}$ (CDCl_3) δ : 7.72–7.65 (m, 1H, arom. H), 7.53–7.46 (m, 2H, arom. H), 7.18–7.12 (m, 3H, arom. H), 7.05–6.99 (m, 2H, arom. H), 6.84 (s, 1H, arom. H), 6.75 (d, $J=11.78$ Hz, 1H, arom. H), 6.51–6.45 (m, 2H, arom. H), 3.50–3.45 (m, 2H, CH_2), 1.66–1.61 (m, 3H, CH_2), 1.38–1.27 (m, 11H, CH_2), 0.88 (t, $J=9.09$ Hz, 3H, CH_3). $^{13}\text{C NMR}$ (CDCl_3) δ : 144.88, 143.31, 136.47, 132.07, 131.93, 131.43, 129.04, 128.91, 128.58, 128.35, 127.90, 123.87, 122.04, 121.24, 118.18, 118.01, 112.94, 111.90, 111.23, 111.04, 44.19, 31.79, 27.83, 27.10, 26.85, 24.91, 22.61, 14.06, 13.56. Anal. Calc. for $\text{C}_{29}\text{H}_{31}\text{NOS}_2$: C, 73.58; H, 6.55; N, 2.96; O, 3.38; S, 13.53. FTMS-ESI (m/z): [M^+] calc. for $\text{C}_{29}\text{H}_{31}\text{NOS}_2$, 473.21.

*Selected data for 3,7-bis(2-thiophene)-*N*-hexadecylphenoxazine 2c* Y=60% (0.42 g), greenish crystals, mp. 69–70°C, $^1\text{H NMR}$ (CDCl_3) δ : 7.69–7.63 (m, 2H, arom. H), 7.46 (d, $J=6.85$ Hz, 2H, arom. H), 7.17 (d, $J=4.94$ Hz, 2H, arom. H), 7.01 (d, $J=3.74$ Hz, 2H, arom. H), 6.89–6.81 (m, 2H,

arom. H), 6.47 (s, 2H, arom. H), 3.49–3.44 (m, 2H, CH₂), 1.57–1.54 (m, 2H, CH₂), 1.34–1.15 (m, 26H, CH₂), 0.87 (t, $J=6.62$ Hz, 3H, CH₃). ¹³C NMR (CDCl₃) δ : 144.85, 143.28, 132.87, 132.12, 131.97, 131.48, 129.08, 128.97, 128.58, 128.42, 127.90, 123.90, 122.06, 121.25, 118.06, 112.94, 111.92, 111.21, 111.01, 32.27, 30.07, 30.03, 29.95, 29.73, 27.19, 23.01, 14.37. Anal. Calc. for C₃₆H₄₅ONS₂: C, 75.66; H, 7.88; O, 2.80; N, 2.45; S, 11.21. FTMS-ESI (m/z): [M⁺] calc. for C₃₆H₄₅ONS₂, 571.21.

3,7-Bis(2-furane)-N-alkylphenoxazine (3a-c)

3,7-Bis(2-furane)-N-alkylphenoxazine (3a-c) Monomer (3) was synthesized according to our previous experience [22, 23] and procedure of obtaining monomers 2a-c, by a coupling condensation of 3,7-dibromo-N-alkylphenoxazine 1 (1.76 mmol) and 2-(tributylstannyl)furane (4.06 mmol).

Selected data for 3,7-bis(2-furane)-N-butylphenoxazine 3a Y=62% (0.40 g), brown oil, ¹H NMR (CDCl₃) δ : 7.69–7.63 (m, 2H, arom. H), 7.47 (d, $J=2.45$ Hz, 2H, arom. H), 7.44 (d, $J=5.75$ Hz, 2H, arom. H), 6.92 (d, $J=8.33$ Hz, 2H, arom. H), 6.42 (d, $J=3.06$ Hz, 2H, arom. H), 6.08 (s, 2H, arom. H), 3.50–3.45 (m, 2H, CH₂), 1.61–1.53 (m, 2H, CH₂), 1.46–1.38 (m, 2H, CH₂), 1.00 (t, $J=7.25$ Hz, 3H, CH₃). ¹³C NMR (CDCl₃) δ : 144.82, 144.52, 144.30, 141.48, 133.34, 132.07, 131.94, 131.82, 131.79, 128.71, 128.52, 128.36, 124.95, 119.27, 118.18, 118.02, 111.80, 111.54, 111.04, 110.91, 43.97, 26.76, 20.09, 13.87. Anal. Calc. for C₂₄H₂₁NO₃: C, 77.63; H, 5.66; N, 3.77; O, 12.94. FTMS-ESI (m/z): [M⁺] cald. for C₂₄H₂₁NO₃: 371.21.

Selected data for 3,7-bis(2-furane)-N-nonylphenoxazine 3b Y=55% (0.41 g), brown oil, ¹H NMR (CDCl₃) δ : 7.69–7.63 (m, 2H, arom. H), 7.45 (d, $J=4.95$ Hz, 4H, arom. H), 7.09 (d, $J=2.98$ Hz, 2H, arom. H), 6.84 (s, 2H, arom. H), 6.42 (d, $J=8.72$ Hz, 2H, arom. H), 3.47–3.42 (m, 2H, CH₂), 1.63–1.58 (m, 2H, CH₂), 1.35–1.26 (m, 12H, CH₂), 0.86 (t, $J=6.51$ Hz, 3H, CH₃). ¹³C NMR (CDCl₃) δ : 144.82, 144.52, 144.30, 141.48, 133.34, 132.07, 131.94, 131.82, 131.79, 128.71, 128.52, 128.36, 124.95, 119.27, 118.18, 118.02, 111.80, 111.54, 111.04, 110.91, 44.11, 31.79, 29.50, 29.32, 29.18, 26.80, 24.87, 22.61, 14.07. Anal. Calc. for C₂₉H₃₁NO₃: C, 78.91; H, 7.03; N, 3.18; O, 10.88. FTMS-ESI (m/z): [M⁺] calc. for C₂₉H₃₁NO₃, 441.21.

Selected data for 3,7-bis(2-furane)-N-hexadecylphenoxazine 3c Y=60% (0.57 g), yellow crystals, mp. 149°C, ¹H NMR (CDCl₃) δ : 7.67–7.63 (m, 2H, arom. H), 7.48 (d, $J=9.91$ Hz, 4H, arom. H), 7.46 (d, $J=5.03$ Hz, 2H, arom. H),

7.30 (s, 2H, arom. H), 6.41 (d, $J=4.62$ Hz, 2H, arom. H), 3.49–3.43 (m, 2H, CH₂), 1.86–1.79 (m, 2H, CH₂), 1.77–1.71 (m, 2H, CH₂), 1.41–1.23 (m, 24H, CH₂), 0.88 (t, $J=8.08$ Hz, 3H, CH₃). ¹³C NMR (CDCl₃) δ : 144.88, 143.31, 136.47, 132.07, 131.93, 131.43, 129.04, 128.91, 128.58, 128.35, 127.89, 123.86, 122.04, 121.24, 118.18, 118.01, 112.94, 111.89, 111.23, 111.04, 44.19, 31.79, 29.66, 29.51, 29.33, 29.19, 29.18, 27.83, 27.10, 26.85, 26.31, 24.91, 22.61, 17.58, 14.06, 13.56. Anal. Calc. for C₃₆H₄₅NO₃: C, 80.15; H, 8.35; N, 2.60; O, 8.90. FTMS-ESI (m/z): [M⁺] calc. for C₃₆H₄₅NO₃, 539.21.

3,7-Bis(2-pyridine)-N-alkylphenoxazine (4a-c)

3,7-Bis(2-pyridin)-N-alkylphenoxazine (4a-c) Monomer (4) as well as 2 and 3 was obtained according to our previous experience [22, 23] by a Stille coupling reaction of 3,7-dibromo-N-alkylphenoxazine 1 (2.52 mmol) with 2-(tributylstannyl)pyridine (5.80 mmol).

Selected data for 3,7-bis(2-pyridin)-N-butylphenoxazine 4a Y=60% (0.59 g), dark red oil, ¹H NMR (CDCl₃) δ : 8.54 (d, $J=4.68$ Hz, 2H, arom. H), 7.57–7.38 (m, 6H, arom. H), 7.27 (s, 2H, arom. H), 7.05–7.00 (m, 2H, arom. H), 6.42 (d, $J=8.40$ Hz, 2H, arom. H), 3.40–3.37 (m, 2H, CH₂), 1.56–1.53 (m, 2H, CH₂), 1.38–1.27 (m, 2H, CH₂), 0.91 (t, $J=7.12$ Hz, CH₃). ¹³C NMR (CDCl₃) δ : 155.96, 149.30, 144.94, 136.50, 133.44, 132.11, 122.13, 121.32, 119.15, 113.51, 111.34, 43.68, 27.11, 20.05, 13.86. Anal. Calc. for C₂₆H₂₃NO₃: C, 79.39; H, 5.85; N, 10.69; O, 4.07. FTMS-ESI (m/z): [M⁺] calc. for C₂₆H₂₃NO₃, 393.01, found, 393.20.

Selected data for 3,7-bis(2-pyridin)-N-nonylphenoxazine 4b Y=54% (0.21 g), dark red oil, ¹H NMR (CDCl₃) δ : 8.60 (d, $J=2.83$ Hz, 2H, arom. H), 7.70–7.64 (m, 2H, arom. H), 7.60–7.57 (m, 2H, arom. H), 7.48 (dd, $J=2.07$ Hz, $J=2.06$ Hz, 2H, arom. H), 7.31 (s, $J=2.06$ Hz, 2H, arom. H), 7.16–7.11 (m, 2H, arom. H), 6.55 (d, $J=8.44$ Hz, 2H, arom. H), 3.57–3.51 (m, 2H, CH₂), 1.75–1.63 (m, 2H, CH₂), 1.39–1.24 (m, 12 H, CH₂), 0.88 (t, $J=7.94$ Hz, 3H, CH₃). ¹³C NMR (CDCl₃) δ : 156.04, 149.26, 136.73, 133.64, 132.08, 122.29, 121.41, 119.35, 113.63, 111.44, 44.10, 31.81, 29.53, 29.37, 29.21, 26.88, 25.04, 22.63, 14.07. Anal. Calc. for C₃₁H₃₃NO₃: C, 80.35; H, 7.13; N, 9.07; O, 3.45. FTMS-ESI (m/z): [M⁺] calc. for C₃₁H₃₃NO₃, 463.21, found, 463.30.

Selected data for 3,7-bis(2-pyridin)-N-hexadecylphenoxazine 4c Y=47% (0.20 g), dark red crystalsl mp. 76°C, ¹H NMR (CDCl₃) δ : 8.61 (d, $J=4.73$ Hz, 2H, arom. H), 7.70–

7.46 (m, 6H, arom. H), 7.31 (s, 2H, arom. H), 7.15–7.11 (m, 2H, arom. H), 6.55 (d, $J=8.43$ Hz, 2H, arom. H), 3.56–3.51 (m, 2H, CH₂), 1.39–1.35 (m, 28H, CH₂), 0.86 (t, $J=7.05$ Hz, 3H, CH₃). ¹³C NMR (CDCl₃) δ : 156.15, 149.37, 145.07, 136.58, 133.61, 132.26, 122.23, 121.39, 119.29, 113.64, 111.42, 76.98, 44.10, 31.89, 29.61, 29.35, 26.88, 25.05, 22.65. Anal. Calc. for C₃₈H₄₇NO₃: C, 81.28; H, 8.38; N, 7.49; O, 2.85. HRMS-ESI (m/z): [M⁺] calc. for C₃₈H₄₇NO₃, 561.01, found, 561.40.

Absorption and fluorescence spectra in dilute solutions

UV-vis absorption spectra were recorded on UV-VIS HP 8452A diode array spectrophotometer in either 1 or 4 cm quartz cuvettes depending on the sample concentration (10⁻⁴–10⁻⁶ mol dm⁻¹). Emission spectra were measured at 295 K in 1 cm long-neck sealed quartz cuvettes using 90° geometry on Hitachi F – 2500 fluorescence spectrophotometer. All solutions were purged with N₂ for 20 min prior measurement. All emission spectra were corrected using correction data obtained with rhodamine and methylene blue as quantum counters for wavelength out to 720 nm, beyond which the response was estimated from the manufacturer's photomultiplier response data.

Cyclic voltammetry

Cyclic voltammetry (CV) studies were performed using an Ecochemie AUTOLAB potentiostat – galvanostat model PGSTAT20 driven by a computer. Samples were dissolved in acetonitrile (CH₃CN for DNA synthesis and peptides), water <10 ppm, POCh, Gliwice, Poland) with 0.1 M tetrabutylammonium tetrafluoroborate Bu₄NBF₄ (Janssen Chimica, 99 %) in acetonitrile as the supporting electrolyte. Solutions were purged with nitrogen gas prior to each scan. A three electrode system was employed using a platinum working and auxiliary electrode. The SCE was served as a reference electrode. The scan rate was 50 mVs⁻¹. Results were analysed using GPES program (*General Purpose Electrochemical System*). Cyclic voltammetry (CV) of electrodeposited film was taken in monomer-free solutions of the same supporting electrolyte as used for polymerization. The voltamograms were referenced to a ferrocene-ferrocenium couple as the standard ($E^{\circ}=0.42$ vs. SCE).

Formation of Langmuir and Langmuir – Blodgett films

Langmuir monomolecular films of desired composition were spread from CHCl₃ solution (concentration of solutions were maintained to ca. 1 mg/ml) on high purity water ($\sigma < 10^{-5}$ S/m) at 296 K. The compression rates used

in experiments ranged between 10 and 20 mm/min, depending on the rigidity of the films. Langmuir – Blodgett deposition was carried out with a KSV System 5000 LB through at the surface pressure of around 25 mN/m. Monomolecular films built of 3,7-bis(thiophene)-*N*-nonylphenoxazine (**2b**) were prepared by means of vertical dipping of the substrate. LB films were deposited at the velocity lower than the draining rate of film of carboxylic acids *i. e.* 1.3 mm/min. After deposition films were stored in vacuum desiccator prior to use. AFM studies of **2b** LB films were carried out using a AFM Dimension V Veeco.

Results and discussion

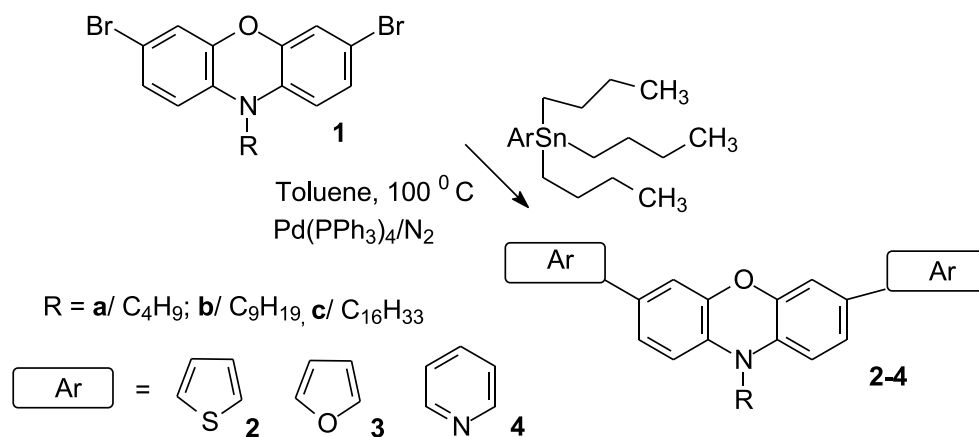
Synthesis

We show that conjugated semiconductors containing the phenoxazine ring have rather low oxidation potentials with some electrochemical reversibility.

The type of condensation, estimated by us as a synthetic procedure (Stille type), has been utilized for the preparation of variety of conjugated aromatic compounds for use in organic light emitting diodes, polymer LEDs and nonlinear optical materials [24]. The cross-coupling reaction of dibromoheterocycle and 2-tributylstannylarylenes catalyzed by palladium phosphine complex is found to provide a efficient, convenient route to conducting compounds. The Stille-type coupling is carried out usually in dry toluene, using palladium compound as catalyst under vigorous stirring at reflux for 24 h. Stille coupling, as well as Suzuki method is also used for obtaining branched or hyperbranched sterically crowded heterocyclic structures. Phenoxazones and phenothiazines because of their non-planar structure (butterfly like) are investigated as optical, electroactive material. Phenoxazine based conjugated system appears in literature as modern optoelectronic systems but not so often as well known phenothiazine blocks [15, 16].

The synthetic route to the phenoxazine based monomers is outlined in Scheme 1. The reaction was run in a way to provide a systematic variation of the phenoxazine derivatives. The monomer 3,7-dibromo-*N*-alkylphenoxazine (**1**) was synthesized according modified procedure reported earlier [13, 20–23], in two steps from the starting phenoxazine with high yield (~70 %). The monomers **2-4**, 3,7-bis(aryl)-*N*-alkylphenoxazines, were prepared (from compound **1**) by palladium-catalyzed Stille coupling with a average yield of ~60 %.

All the synthesized products were soluble in organic solvents such as chloroform, toluene, and tetrahydrofuran (THF). The molecular structures of the monomers were verified by NMR, MS and UV-VIS spectra.

Scheme 1 Synthetic setup for *N*-alkyl-bis(arylene)phenoxazines

Spectroscopic properties

Phenoxazines usually have high luminescence quantum yields and are known as efficient laser dyes. Because of phenoxazine emission's maxima are close to 400 nm, polymers or other conjugated oligomers containing phenoxazine units could be promising conducting and fluorescent materials.

The selection of a hole- and electron-conducting core is dedicated by the HOMO and LUMO energy levels as well as the charge-carrier mobility.

The photophysical properties of some synthesized compounds (**2b**, **4b**) were investigated by UV-VIS and fluorescence spectroscopy in dilute acetonitrile solution (10^{-4} – 10^{-6} M). The UV-VIS absorption and luminescence properties of hyperbranched blocks were summarized in Figs. 2, 3 and 4 as well as in Table 1. Figure 2 shows the UV-VIS absorption spectra of **2b** and **4b**. The 220–320-nm bands in the absorption spectra can be assigned to the $\pi - \pi^*$ transition whereas the 330–440-nm bands are due to ICT (increasing excited-state dipole moments). The compounds have strong featureless absorption bands with an absorption maximum (λ_{\max}) at 382–400 nm in dilute solution. The absorption maxima of **2b** and **4b** are similar to values of λ_{\max} corresponding to the $\pi - \pi^*$ transition in polyphenoxazine backbone [20]. The absorption bands characteristic for phenoxazine ring are localized at about 400 nm.

Compound **2b** has two clear peaks with absorption maxima at 265 and 382 nm. The wide and characteristic band with the maximum at 382 nm is connected with phenoxazine rings but the observed blue-shift suggests that some contribution to the absorption spectrum comes from the thiophene segments.

Similar absorption spectra were found for **4b** (265 and 400 nm), but the absorption maxima are red-shifted about 20 nm in comparison to **2b** (Fig. 2). The red-shifted absorption maxima in these two compounds may be due to the increased electronic delocalization and conformation of

bis-pyridine blocks. Summarized, two prominent absorption features were observed in the spectra of both the D-A molecules: a lowest-energy band in the 330–440 nm range and high-energy bands in the 220–320 nm.

The optical band gap (E_{gap}) derived from the absorption edge of the solution spectra of **2b** and **4b** was in the range of 2.70–2.84 eV (Table 1), the values are differ than it found for polyphenoxazine (2.44 eV [13]) because of presence of side heterocyclic rings.

The fluorescence emission spectra of phenoxazine derivatives in dilute acetonitrile solutions were recorded at different excitation wavelengths in the range of 374–390 nm, but the emission values were the same. However, during excitation of the dilute solution of **2b** at 374 the emission was centred at 436 nm (Fig. 3) whereas **4b**, excited at 390 nm has an emission at 460 nm (Fig. 4), the bands are of almost comparable intensities, but the fluorescence quantum yields of the compound **2b** is slightly smaller than **4b**, which is probably due to the photoinduced intramolecular transfer between two chromophores. On the other hand, it was noticed the similar emission shapes. It may be assumed that emission is connected mainly with

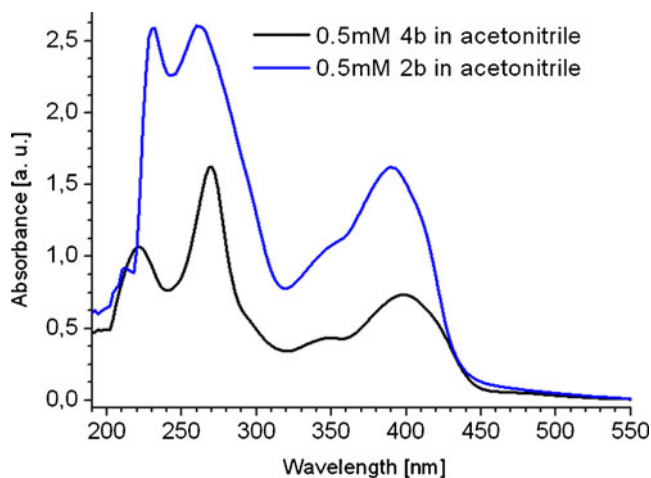
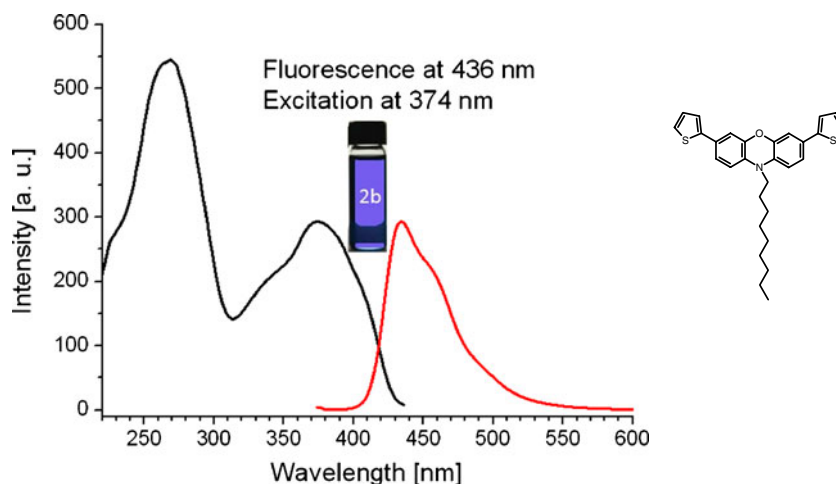
**Fig. 2** UV-VIS spectra of diluted **2b** and **4b** in acetonitrile

Fig. 3 The fluorescence spectra of 1 μ M solution of **2b** in acetonitrile



excitation of the phenoxazine ring. Following excitation into the S_2 band the phenoxazines exhibit $S_2 \rightarrow S_0$ fluorescence. The $S_2 \rightarrow S_0$ fluorescence bands of **2b** and **4b** are located in the region of 430–480 nm, which is considerably red-shifted to the pure nonylphenoxazine fluorescence, which has a maximum at ca. 450 nm (not shown). The $S_2 \rightarrow S_0$ fluorescence band observed for **4b** is also broader than the corresponding emission band of **2b**, with full-width-at-half-maxima of ca. 7,000 and 5,000 cm^{-1} respectively.

The emission spectrum of **4b** dramatically red shifts with increasing electron-accepting strength. Compound **4b** emits a blue color in solution (**2b** – blue-violet). The obvious reason for the observed red shift is characteristic of donor- π -acceptor structure, which may induce solvent polar effects on their maximal absorption wavelength. It is also connected with the greater degree of ICT with increasing electron acceptor strength.

Thus, emission colors spanning the entire visible region are obtained from the phenoxazine-based D-A molecules, demonstrating how charge transfer and the resultant ICT

fluorescence in a D-A molecule can be effectively manipulated through the electronaccepting strength of the acceptor building block.

Electrochemical properties

To understand the electronic structures of the phenoxazine derivative molecules, we performed cyclic voltammetry (CVs) measurements.

Experimental results and theoretical calculations suggest that 5 and 5' (Fig. 1) positions in five-membered heterocyclic ring are characteristic places for electrochemical polymerization [25]. The polymerization leads to copolymer with alternate phenoxazine and biheterocyclic groups (e.g. thiophene) in the main chain.

Cyclic voltammograms of compounds (**2b**, **4b**) in acetonitrile are shown in Figs. 5, 6 and 7. The electronic states (HOMO/LUMO levels) of the polyphenoxazine homopolymer [13] as well as synthesized 3,7-bis(2-thiophene/pyridine)-*N*-nonylphenoxazines (**2b**, **4b**) did not show a reduction wave in the range from -0.5 –

Fig. 4 The fluorescence spectra of 10 μ M solution of **4b** in acetonitrile

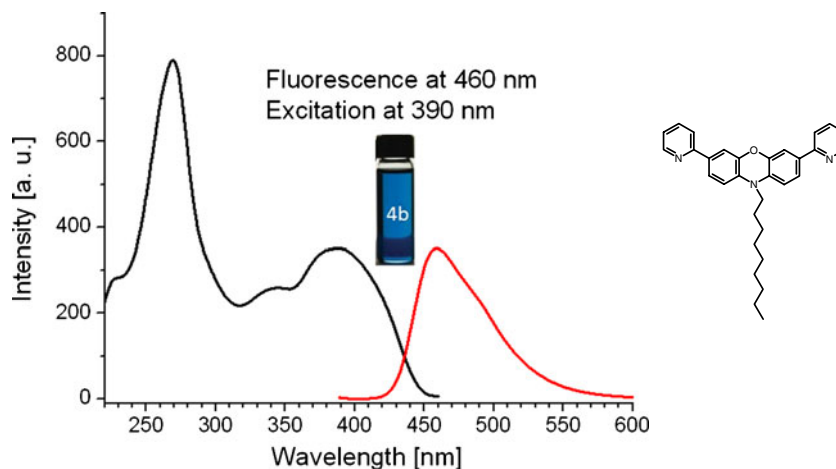


Table 1 Summary of physical properties of phenoxazine derivatives

compound	in acetonitrile solution (5×10^{-4} – 10^{-4} M)		E_{gap}^b [eV]	E_{gap}^c [eV]
	abs λ_{max} [nm]	Em λ_{max}^a [nm]		
2b	382	436	3.54	2.84
4b	400	460	3.43	2.70

0.0 V, suggesting a *p*-type semiconducting material in case of polyphenoxazine.

The following discussion is focused on the electrochemical oxidation of bis(aryl)-*N*-alkylphenoxazines, which occurs apparently in several steps and seems to be quite complicated. The CVs of the molecules **2b**, **4b** (Figs. 5, and 6) can be repeatedly scanned many cycles in the range -0.5 – 1.4 V (*vs* SCE). The monomer **2b** (Fig. 5) as well as **4b** (Fig. 6) has rather clear oxidation waves (especially noticeable in case of **2b**), that are not always reversible, highly reversible is only the first redox system for **2b** and **4b**, as evident from the areas and close proximity of the anodic and cathodic peaks.

According to the possibility of obtaining copolymers of the synthesized phenoxazine structures, it is crucial to mention that the homopolymer of phenoxazine [20] has an onset oxidation potential of 0.36 V (*vs* SCE), from which was estimated an ionization potential of 4.8 eV. The IP values found for phenoxazine copolymers were very similar ~ 4.7 eV (Table 2). The 4.8 eV IP value for the phenoxazine – thiophene block is hardly less than poly(3-hexylthiophene) (4.9 eV [13]). These results suggest that the phenoxazine ring is a building block for lowering the IP of conjugated copolymers or oligomers. The reversible electrochemical oxidation and low IP of phenoxazine and

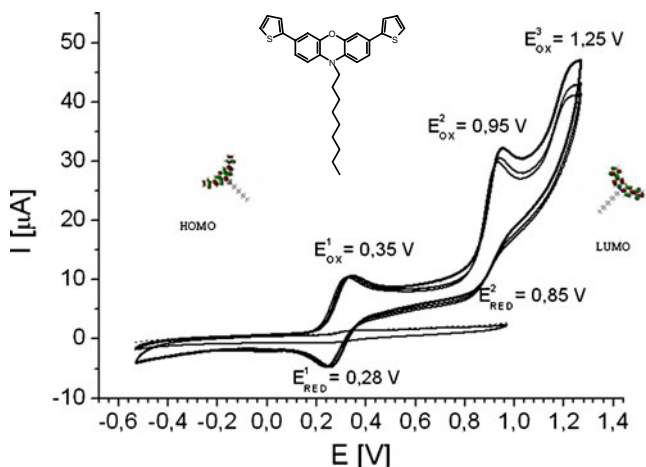


Fig. 5 Cyclic voltammety of 3,7-bis(2-thiophene)-*N*-nonylphenoxazine (**2b**) in 0.1 mM solution of 0.1 M Bu_4NBF_4 in acetonitrile. Potential sweep rate $\nu=50$ mV/s

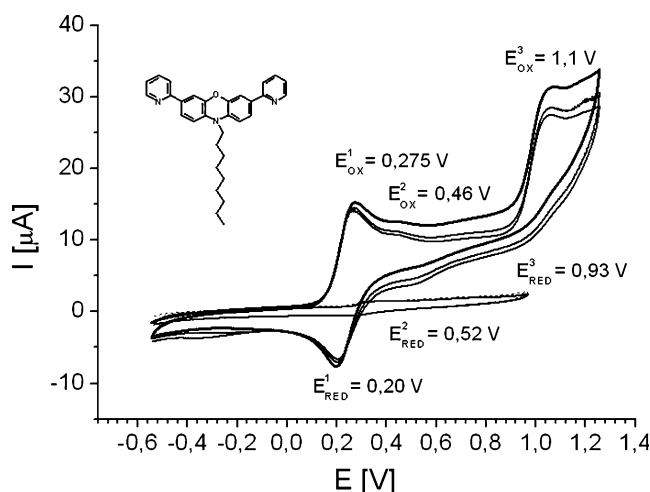


Fig. 6 Cyclic voltammety of 3,7-bis(2-pyridine)-*N*-nonylphenoxazine (**4b**) in 0.1 mM solution of 0.1 M Bu_4NBF_4 in acetonitrile. Potential sweep rate $\nu=50$ mV/s

its copolymers suggest the efficient hole injection and transport with regard to gold, which is commonly used as the source and drain electrodes in organic field transistors.

Repetitive scanning of the monomer **2b** solution within the specific potential range results in uniform and coherent film formation on the electrode surface (Fig. 7). The polymeric film formation is evidenced by the successive growth of the current within the 0.2–1.2 V potential range. Electrochemical polymer films built stable homogeneous layers on PT electrode.

In the case of **2b** molecule despite presence of thiophene rings, in first cycle we do not observe polymerization of radical cation, because this process is connected with dication. Analysis of successive voltammetric cycles allow to claim that during 20 cycles first redox system does not change (Fig. 7) therefore every next cycle displace

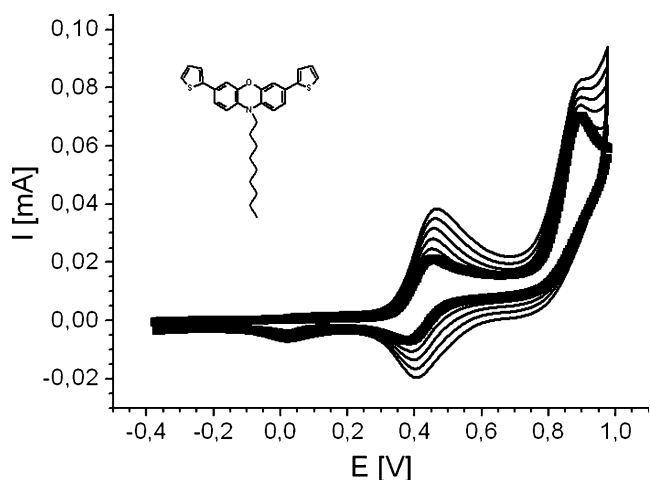


Fig. 7 Cyclic voltammety of **2b** in 0.1 M solution of Bu_4NBF_4 in acetonitrile. Potential sweep rate $\nu=50$ mV/s; 30 scans

Table 2 Redox properties of phenoxazine derivatives

compound	IP (eV) ^a
2b	4.75
4b	4.68

maximum of first oxidation peak to higher potentials, results in lower first oxidation peak and disappearing proper reduction peak.

Results of CV measurements (Fig. 8) suggest that shape of CV curves is dependent on thickness of polymer film.

In case of thick polyphenoxazine film we observed total demise of electroactivity phenoxazine radical cation's redox system, whereas there is new oxidation peak in 0.78 V. This type of behaving is connected with structure of the main polymer chain (Fig. 1).

Butterfly like structure of phenoxazine derivative makes difficult delocalization of charge on conjugated chain, in this case electron can not move along polymer backbone. Observed first redox process is at 0.28 V and is connected with electron transfer between phenoxazines of neighbored polymer chains.

Transfer velocity of electrons depends on distances between phenoxazine mers and decreases with increasing of disorder in main backbones.

Deficiency in polymer order is connected with film thickness, then is observed considerable remission of first redox couple (Fig. 8), connected with phenoxazine units dismissing from electrode surface. As the electrode potential finds enough value to oxidize bithiophenes, positive charge of polymer is also able to free moving along the polymer backbone and between neighbored chains, then polymer behaves as an electroconducting material. Such a situation confirms the phenoxazines oxidize by oxidized bithiophene units.

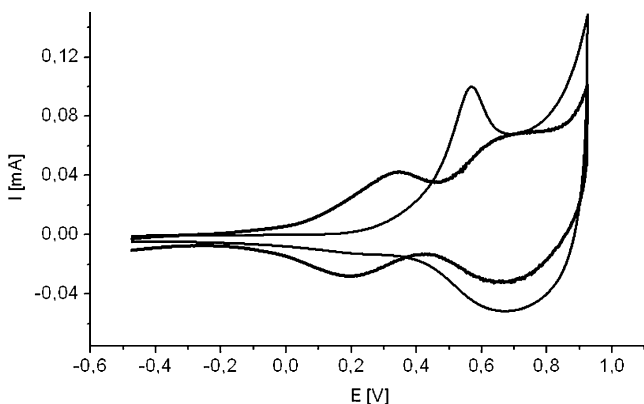


Fig. 8 Cyclic voltammery of poly-**2b** film in 0.1 M solution of Bu_4NBF_4 in acetonitrile. Potential sweep rate $\nu=50$ mV/s. 1—film synthesized in 10 voltammetric cycles, 2—film synthesized in 30 voltammetric cycles. Both cycles were normalized according maximum of second redox system peak

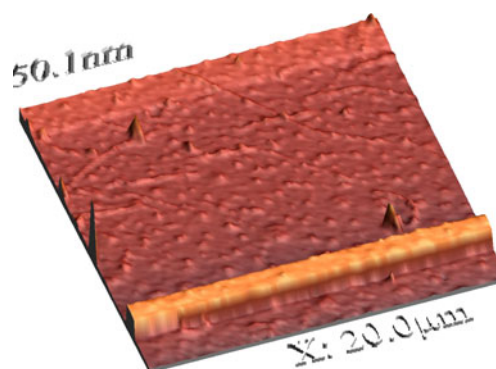


Fig. 9 AFM image of active layer of **2b** LB film (20 layers) on glass slide, top view

Characteristic of thin Langmuir-Blodgett films

The technique of Langmuir-Blodgett was also employed to obtain thin molecular film of bis(thiophene)phenoxazines. In this connection, phenoxazine derivative - *N*-nonyl-3,7-bis(2-thiophene)phenoxazine, dissolved in organic solvents (chloroform) was spread on the water. Then organic layers were deposited by LB technique onto a set of eight interdigital, buried Au electrodes photolithographically fixed on SiO_2 thermally coated silicon substrates or on silicon substrates.

Langmuir monomolecular films of phenoxazine derivatives **2b**—was spread from CHCl_3 solution on high purity water. LB deposition was carried out with a KSV System 5000 LB trough at a surface pressure of around 25 mN/m.

The deposition processes were carried out at room temperature as well as conductivity measurements. The transference of LB film was Y—type in first deposition and Z—type in following ones. The relationship between absorbance and number of layers and constant transfer ratio during the deposition indicated a constant architecture of LB film layers.

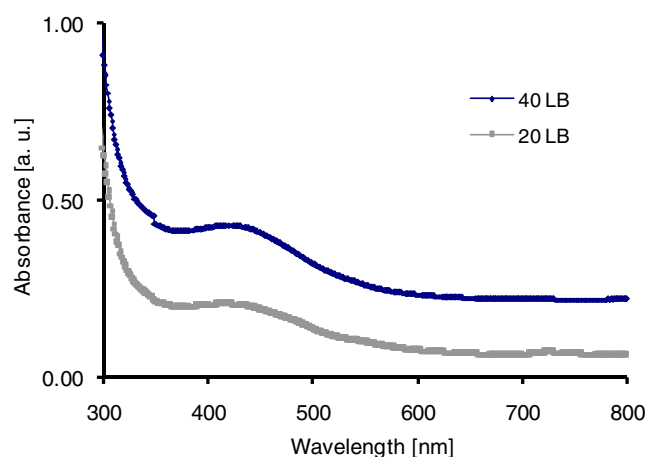


Fig. 10 Normalized optical absorption spectra of phenoxazine derivative **2b** as thin films on silica substrates

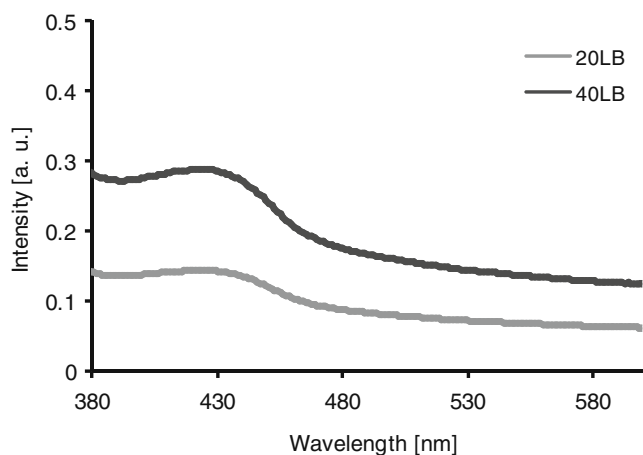
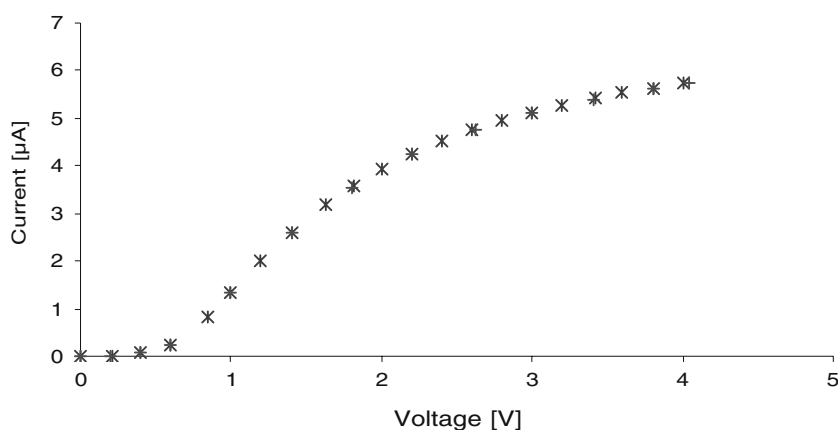


Fig. 11 Normalized fluorescence spectra of phenoxazine derivative **2b** as thin films on silica substrates, Ex. 374 nm

The morphology of LB layers of phenoxazine derivative was examined using atomic force microscopy (AFM). Figure 9 shows the tapping-mode AFM images of Langmuir – Blodgett layers on silicon slides. The homogeneous films average roughness is not very high for an LB film. The roughness of **2b** was measured as 4.9 nm, it is probably due to reorganization of big molecule of **2b**. In fact, a rather high degree of homogeneity is observed for the film, layers are rather compact and well-organized.

The normalized optical absorption spectra of the phenoxazine conjugated derivative **2b** as thin films are shown in Fig. 10. The absorption spectra of thin films of these compounds are generally similar in shape to those in dilute solutions. The lowest energy $\pi - \pi^*$ transition is centered at 440 nm while an additional higher energy band is found at 303 nm. The absorption maximum of **2b** is clearly red-shifted to 440 nm compared to dilute solution (382 nm). The red-shifted absorption maximum in case of thin LB film of **2b** is due to a more planar conformation in the solid state. The similarity in terms of spectral shapes between the thin film absorption spectra and dilute solution spectra suggests comparable ground-state electronic structures of

Fig. 12 The current—voltage characteristics of 20 layer LB film built of 3,7-bis(2-thiophene)-*N*-nonylphenoxazine (**2b**)



compound with no significant change in conformation in the condensed state.

Figure 11 shows the fluorescence emission spectra of the thin LB film of **2b**. In the solid state, the emission maxima of many conjugated polymers are usually red-shifted by 13–23 nm relative to those in solution [13]. The spectrum of LB film of **2b** shows the emission peak at 448 nm.

An investigations of the electrical conductivity of LB films consisting twenty monolayers of 3,7-bis(2-thiophene)-*N*-nonyl -phenoxazine (**2b**) a potential precursors of the new conducting polymers were carried out with *Keithley 614* electrometer.

Figure 12 shows typical *I-V* curves of fabricated 20-layers LB films at room temperature. The *I-V* curves are asymmetric and non-linear. The forward currents follow approximately an exponential trend. This *I-V* behaviour is connected with typical semiconducting properties.

The current flowing through as—deposited films in most cases ranged between $6 \cdot 10^{-6}$ A and $1.2 \cdot 10^{-7}$ A at room temperatures, furthermore the current apparently increasing during exposure on white light. There was found also the estimated conductivity, $\sigma = 1.4 \cdot 10^{-6}$ S/m.

Therefore, these results indicate that the obtained films behave as semiconductor.

Conclusions

In summary, we have demonstrated a synthesis of series new phenoxazine-based molecules. The main purposes of investigation were also electrochemical and photophysical properties of designed electro-donor/acceptor tricyclic units. The obtained, amphiphilic phenoxazine structures seemed to be a valuable tool to allow both fabrication of multilayer conducting devices with modest carrier mobility, and some materials with optical properties.

The synthesized molecules opens a broad window of transmission in the blue region of the visible spectrum. Tricycles phenoxazine molecules exhibit rather reversible

electrochemical oxidation and reduction, indicating ambipolar redox properties that could facilitate efficient hole/electron injection, transport, and charge recombination. The phenoxazine-based molecules have low ionization potentials (4.68–4.75 eV) characteristic for conducting structures. Overall, these studies offer a viable approach to semiconducting material with high stability and usability.

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