



# Diaza-analogs of benzopyrene and perylene containing thienyl and 4-(phenylamino)phenyl groups: Synthesis, characterization, optical and electrochemical properties



Denis S. Baranov<sup>a, b</sup>, Mikhail N. Uvarov<sup>a, \*</sup>, Maxim S. Kazantsev<sup>b, c</sup>,  
Evgeny A. Mostovich<sup>b, c</sup>, Evgeni M. Glebov<sup>a, b</sup>, Yurii V. Gatilov<sup>b, c</sup>, Leonid V. Kulik<sup>a, b</sup>

<sup>a</sup> V.V. Voevodsky Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Science, 630090 Novosibirsk, Russian Federation

<sup>b</sup> Novosibirsk State University, 630090 Novosibirsk, Russian Federation

<sup>c</sup> N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Science, 630090 Novosibirsk, Russian Federation

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## ABSTRACT

Series of 1,8-diazabenzopyrenes and 1,7-diazaperylenes with thienyl or 4-(phenylamino)phenyl groups were designed and synthesized by a one-pot process from the functionalized terminal alkynes and either 1,4- or 1,5-diiodoanthraquinones in order to investigate the effect of extending  $\pi$ -conjugation at the 2,7- and 2,8-positions on the optical and electrochemical properties. The substances synthesized were characterized by X-ray analysis, cyclic voltammetry, UV–vis and luminescence spectroscopy. Energies and spin-densities of frontier molecular orbitals were calculated by DFT. Practically planar crystal structures of 1,8-diazabenzopyrene and 1,7-diazaperylene with thienyl groups were confirmed by X-ray diffraction data. Solid-state luminescence was obtained for the synthesized substances in drop-casted films and in 1,4-dioxane/water mixtures.

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## 1. Introduction

Organic polycondensed materials such as chemically modified pyrenes and perylenes [1] could be applied in organic electronics [2,3], in particular, in planar- and bulk-heterojunction organic photovoltaic devices as acceptor [4–6] or donor [7] small molecules, as light absorber in dye-sensitized solar cells [8] and as semiconducting materials in organic field-effect transistors [9–13]. In some cases significant changes of optical properties and fluorescence quantum yield of such substances arise from even apparent insignificant chemical modifications of the molecules [14–16]. Moreover surrounding media could change color and fluorescence intensity dramatically which allows the application of such substances as chemosensors for metal ions in solutions [17–20] and as fluorescent indicators of solvent polarity and pH sensors [21,22]. High values of luminescence yields allow to use such polycondensed molecules in emitting layers of organic light emitting devices [20,23–27].

Previously, we have presented a synthetic route to obtain

diazaperylenes [28] and diazabenzopyrenes [29] containing aliphatic substituents. In this synthetic route the main chemical transformations were based on annulation of the two pyridine rings to the anthraquinone core by reaction of the bis(*R*-ethynyl) anthraquinones with urea in DMF. Note that this synthetic approach is quite simple and does not require organometallic compounds or aggressive conditions. New aza-analogues of perylene and benzopyrene containing thienyl and 4-(phenylamino)phenyl groups are promising for organic electronic applications because thienyl  $\pi$ -conjugated group is the most popular building unit for organic semiconductor materials and phenylamines are widely used in light-emitting diodes as hole-transporting and emissive layers [30].

In the present paper we report a one-pot synthesis of new aza-analogues of perylene and benzopyrene containing thienyl and 4-(phenylamino)phenyl groups. The synthesized substances were characterized by X-ray analysis, cyclic voltammetry, UV–vis and luminescence spectroscopy to indicate possible applications of these materials.

\* Corresponding author.

E-mail address: [uvarov@kinetics.nsc.ru](mailto:uvarov@kinetics.nsc.ru) (M.N. Uvarov).

## 2. Experimental

### 2.1. General

Elemental analyses were performed with a CHN-analyzer (Model 1106, 'Carlo Erba', Italy). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AV-400 spectrometer. Melting points were determined with a Kofler apparatus. Mass spectra were measured on a Thermo Electron Corporation DFS mass spectrometer (70 eV), using direct injection, the temperature of the ionization chamber was 220–270 °C. The IR-spectra were recorded on a Shimadzu IRTracer-100 instrument with GS10802-X Quest ATR ZnSe Accessory (Specac). Cyclic voltammetry (CVA) measurement were performed in  $\text{CH}_2\text{Cl}_2$  solution on a computer controlled P-8nano potentiostat/galvanostat (Elins) in combination with three-electrode cell (Gamry), 0.1 M tetrabutylammonium hexafluorophosphate being used as supporting electrolyte. The Pt-disc, Pt wire and Ag/AgCl were used as working, counter and reference electrode respectively. The reference electrode was calibrated by measuring the redox potentials of ferrocene.

The HOMO and LUMO energy levels were estimated using onset oxidation and reduction potentials measured vs  $\text{Fc}/\text{Fc}^+$  in the cyclic voltammograms according to Eqs. (1) and (2):

$$E_{\text{homo}} = -e(E_{\text{ox}}^{\text{onset}} + 4.8) \text{ (eV)} \quad (1)$$

$$E_{\text{lumo}} = -e(E_{\text{red}}^{\text{onset}} + 4.8) \text{ (eV)} \quad (2)$$

Column chromatography was performed on alumina (50–150  $\mu\text{m}$ , TU 6-09-3916-75) and the Kieselgel 60 plates (Merck) were used for TLC analysis. All reagents were purchased from commercial chemical suppliers.

For preliminary geometry optimization semi-empirical AM1 from MOPAC 2012 was used [31]. Final geometry optimization step was done with ORCA 3.0.1 [32] package by DFT B3LYP using a balanced polarized triple-zeta basis set def2-TZVP [33,34]. All visualizations were done by using Gabedit 2.4.8 software [35]. All DFT calculations were performed using Siberian Supercomputing Center [36].

The UV–Vis absorption spectra were recorded using an Agilent 8453 spectrophotometer (Agilent Technologies), and luminescence spectra were recorded using FLSP-920 spectrofluorimeter (Edinburgh Instruments) in toluene, 1,4-dioxane (dioxane) or dioxane/water mixture solutions with the concentrations  $10^{-5}$  M. Excitation at 375 nm was used to record luminescence spectra and kinetics. The solutions in dioxane/water mixtures were prepared by adding of water into dioxane. Molar absorption coefficients  $\epsilon$  were determined at maximum absorption in the visible spectral region. Photoluminescence quantum yield  $\phi$  values were determined using the ethanol solution of Coumarine 153 as standard ( $\phi_{\text{C153}} = 0.38$ ) [37].

The analytical and spectroscopic investigations were carried out at the Multi-Access Chemical Service Center of the Siberian Branch of the Russian Academy of Sciences. XRD data for compounds **8b**, **9b** were obtained on a Bruker Kappa Apex II CCD diffractometer using  $\phi$ ,  $\omega$  scans of narrow ( $0.5^\circ$ ) frames with Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and a graphite monochromator at room temperature.

### 2.2. Synthesis

#### 2.2.1. *N*-octyldiphenylamine (1)

A mixture of diphenylamine (10 g, 0.056 mol), octyl bromide (12 g, 0.062 mol), benzyltriethylammonium chloride (BTEAC) (1.4 g, 6.0 mmol), NaOH (12 g, 0.3 mol) and  $\text{H}_2\text{O}$  (10 mL) was vigorously stirred for 24 h at reflux temperature (Scheme 1). After cooling, the

organic layer was separated. The crude product was purified by column chromatography on alumina (elution with petroleum ether). Yield 14.4 g (87%), colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.88 (3H, t,  $J$  6.9 Hz, Me), 1.28 (10H, m,  $(\text{CH}_2)_5$ ), 1.66 (2H, m,  $\text{CH}_2$ ), 3.68 (CH, t,  $J$  7.8 Hz,  $\text{NCH}_2$ ), 6.94 (2H, m,  $\text{H}_{\text{Ar}}$ ), 6.99 (4H, m,  $\text{H}_{\text{Ar}}$ ), 7.26 (4H, m,  $\text{H}_{\text{Ar}}$ ) ppm ( $^1\text{H}$  NMR Ref. [38]).

#### 2.2.2. 4-Iodo-*N*-octyldiphenylamine (2)

Powdered iodine (11.6 g, 0.046 mol) was added portions over 0.5 h to a vigorously stirred mixture of the diphenylamine **1** (13 g, 0.046 mol),  $\text{KHCO}_3$  (7 g, 0.07 mol) and  $\text{H}_2\text{O}$  (40 mL) at room temperature. The reaction mixture at room temperature was stirred for 2 h. After ethyl acetate (100 mL) was added, the organic layer was washed with solution  $\text{Na}_2\text{SO}_3$ , dried over  $\text{MgSO}_4$  and concentrated on rotary evaporator. The crude product was purified by column chromatography on alumina (elution with petroleum ether). Yield 9.8 g (52%), colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.88 (3H, t,  $J$  6.9 Hz, Me), 1.28 (10H, m,  $(\text{CH}_2)_5$ ), 1.63 (2H, m,  $\text{CH}_2$ ), 3.64 (2H, t,  $J$  7.8 Hz,  $\text{NCH}_2$ ), 6.66 (2H, dt,  $J$  3.1, 8.9 Hz,  $\text{H}_{\text{Ar}}$ ), 7.05 (3H, m,  $\text{H}_{\text{Ar}}$ ), 7.30 (2H, m,  $\text{H}_{\text{Ar}}$ ), 7.47 (2H, dt,  $J$  3.1, 8.9 Hz,  $\text{H}_{\text{Ar}}$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 14.25, 22.77, 27.17, 27.40, 29.42, 29.51, 31.93, 52.46 ( $\text{C}_8\text{H}_{17}$ ), 81.46 (C), 120.79 (2CH), 123.03 (CH), 123.38 (2CH), 129.63 (2CH), 137.95 (2CH), 147.47 (C), 148.05 (C) ppm. HMRS, found:  $[\text{M}+\text{H}]^+ m/z$  407.1107;  $\text{C}_{20}\text{H}_{26}\text{NI}$   $[\text{M}+\text{H}]^+$  407.1104.

#### 2.2.3. 1-((4-(Octyl(phenyl)amino)phenyl)ethynyl)cyclopentanol (3)

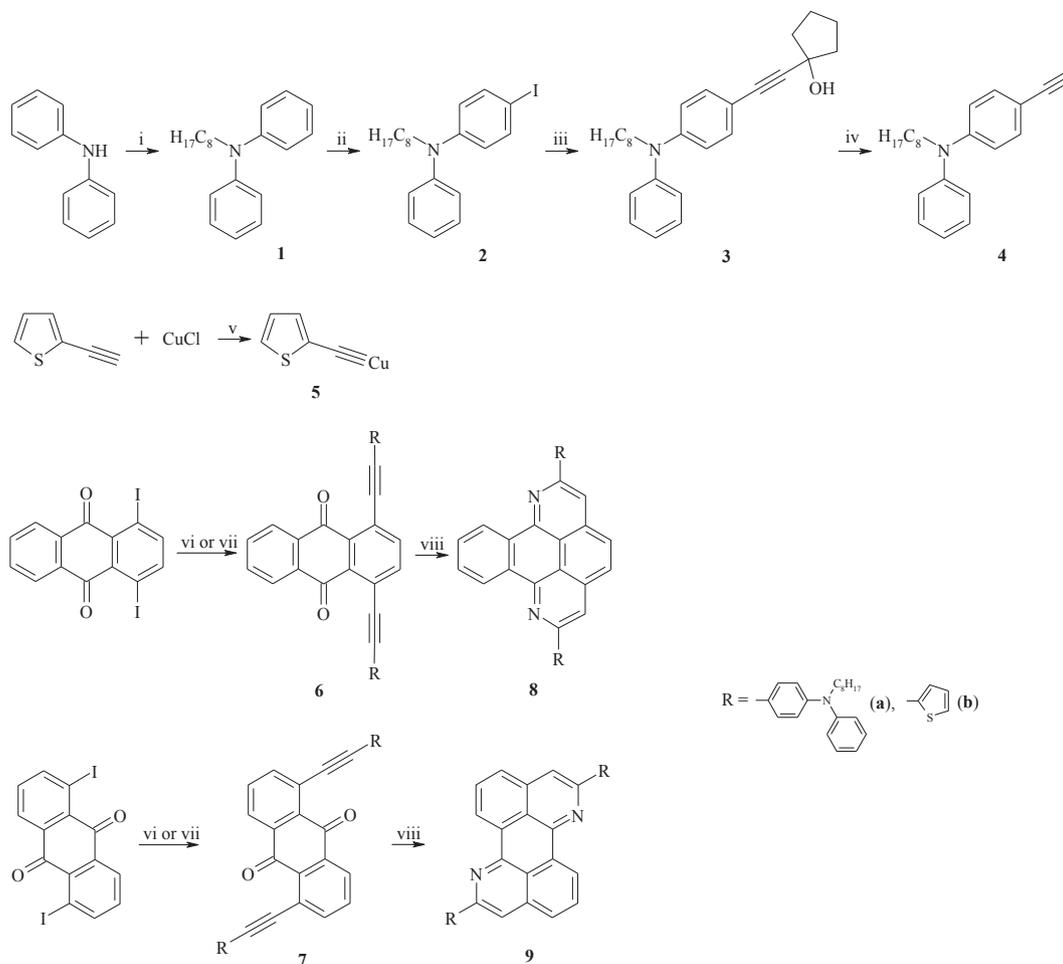
Under argon, a mixture of the iodide **2** (8.6 g, 0.021 mol), 1-ethynylcyclopentanol (3.3 g, 0.03 mol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (40 mg, 0.056 mmol), CuI (20 mg, 0.1 mmol),  $\text{Na}_2\text{CO}_3$  (3 g, 0.028 mol),  $\text{H}_2\text{O}$  (3 mL) and  $\text{Et}_2\text{NH}$  (8 mL) in 30 mL of toluene was stirred for 3 h at 80 °C. After cooling, the organic layer was washed with water (250 mL), dried over  $\text{MgSO}_4$ . The crude product was purified by column chromatography on alumina (elution with toluene). Yield 7.5 g (92%), light yellow oil. IR (neat,  $\text{cm}^{-1}$ ): 2953, 2924, 2855 (Alk), 2220 ( $\text{C}\equiv\text{C}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.87 (3H, t,  $J$  6.9 Hz, Me), 1.27 (10H, m,  $(\text{CH}_2)_5$ ), 1.64 (2H, m,  $\text{CH}_2$ ), 1.78 (2H, m,  $\text{CH}_2$ ), 1.86 (2H, m,  $\text{CH}_2$ ), 2.02 (4H, m,  $(\text{CH}_2)_2$ ), 3.66 (2H, t,  $J$  7.8 Hz,  $\text{NCH}_2$ ), 6.75 (2H, dt,  $J$  2.7, 8.7 Hz,  $\text{H}_{\text{Ar}}$ ), 7.09 (3H, m,  $\text{H}_{\text{Ar}}$ ), 7.25 (2H, dt,  $J$  2.7, 8.7 Hz,  $\text{H}_{\text{Ar}}$ ), 7.32 (2H, m,  $\text{H}_{\text{Ar}}$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 14.25, 22.77, 23.65 (2C), 27.16, 27.45, 29.41, 29.51, 31.93, 42.74 (2C), 52.44, 75.20 (Alk), 83.71, 91.23 ( $\text{C}\equiv\text{C}$ ), 112.71 (C), 117.10 (2CH), 123.59 (CH), 124.44 (2CH), 129.66 (2CH), 132.70 (2CH), 147.31 (C), 148.22 (C) ppm. Found: C, 82.86; H, 8.72; N, 3.50%;  $\text{C}_{27}\text{H}_{35}\text{NO}$  C, 83.24; H, 9.06; N, 3.60%. HMRS, found:  $[\text{M}+\text{H}]^+ m/z$  389.2708;  $\text{C}_{27}\text{H}_{35}\text{NO}$   $[\text{M}+\text{H}]^+$  389.2713.

#### 2.2.4. 4-Ethynyl-*N*-octyldiphenylamine (4)

To a solution of the alkynol **3** (2 g, 5.1 mmol) in dry toluene (10 mL) anhydrous powdered KOH was added (400 mg, 7.1 mmol), and the mixture was stirred at reflux for 0.5 h. After cooling, petroleum ether (20 mL) was added and the reaction mixture was flash chromatographed on alumina (elution with petroleum ether). Yield 1.3 g (83%), light yellow oil. IR (neat,  $\text{cm}^{-1}$ ): 3304 ( $\equiv\text{CH}$ ), 2953, 2922, 2853 ( $\text{C}_8\text{H}_{17}$ ), 2102 ( $\text{C}\equiv\text{C}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 0.88 (3H, t, Me,  $J$  6.9 Hz), 1.28 (10H, m,  $(\text{CH}_2)_5$ ), 1.65 (2H, m,  $\text{CH}_2$ ), 2.99 (1H, s,  $\equiv\text{CH}$ ), 3.67 (2H, t,  $J$  7.8 Hz,  $\text{NCH}_2$ ), 6.73 (2H, dt,  $J$  2.7, 9.0 Hz,  $\text{H}_{\text{Ar}}$ ), 7.12 (2H, m,  $\text{H}_{\text{Ar}}$ ), 7.33 (4H, m,  $\text{H}_{\text{Ar}}$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 14.24, 22.77, 27.16, 27.45, 29.41, 29.51, 31.93, 52.48 ( $\text{C}_8\text{H}_{17}$ ), 75.41 ( $\equiv\text{CH}$ ), 84.60 ( $-\text{C}\equiv$ ), 111.40 (C), 116.37 (2CH), 124.14 (CH), 125.16 (2CH), 129.76 (2CH), 133.23 (2CH), 147.11 (C), 148.73 (C) ppm. Found: C, 86.36; H, 9.08; N, 4.42%;  $\text{C}_{22}\text{H}_{27}$  N C, 86.51; H, 8.91; N, 4.59%.

#### 2.2.5. Copper (I) thien-2-ylacetylde (5)

A mixture of CuCl (4.2 g, 0.042 mol),  $\text{NH}_4\text{Cl}$  (8.8 g, 0.1 mol),



**Scheme 1.** Reagents and conditions: i,  $C_8H_{17}Br$ , BTEAC, NaOH,  $H_2O$ , reflux, 24 h; ii,  $I_2$ ,  $KHCO_3$ ,  $H_2O$ , r. t., 2 h; iii, 1-ethynylcyclopentanol,  $PdCl_2(PPh_3)_2$ , CuI,  $Na_2CO_3$ ,  $Et_3NH$ ,  $H_2O$ , PhMe,  $80^\circ C$ , 3 h; iv, KOH, PhMe, reflux, 0.5 h; v, CuCl,  $NH_4Cl$ ,  $NH_3$ ,  $NH_2OH \cdot HCl$ ,  $H_2O$ , r. t., 5 h; vi, Alkyne **4**,  $PdCl_2(PPh_3)_2$ , CuI,  $Et_3N$ , PhMe,  $75^\circ C$ , 9 h; vii, copper acetylide **5**, Py,  $65^\circ C$ , 0.5 h; viii,  $(NH_2)_2CO$ , DMF, reflux, 14–18 h.

$NH_2OH \cdot HCl$  (0.9 g, 0.013 mol), 25% aqueous  $NH_3$  (21 mL) in  $H_2O$  (160 mL) was stirred at room temperature under argon atmosphere. After stirring for 20 min, 2-ethynylthiophene (3.6 g, 0.033 mol) was added into the mixture over a period of 1 h. After stirring the reaction mixture for a further 4 h, the yellow precipitate copper acetylide was filtered, washed with EtOH, and dried in vacuum. Yield 5.25 g (94%).

#### 2.2.6. Synthesis of bis(R-ethynyl)-9,10-anthraquinones (general procedure)

Under argon, a mixture of diiodo-9,10-anthraquinone (500 mg, 1.1 mmol), the alkyne **4** (920 mg, 3.0 mmol),  $PdCl_2(PPh_3)_2$  (20 mg, 0.028 mmol), CuI (10 mg, 0.052 mmol),  $Et_3N$  (2 mL) in toluene (15 mL) was stirred for 8–9 h at  $75^\circ C$ . Then the reaction mixture was cooled, solvent was evaporated on rotary evaporator and was chromatographed on alumina (elution with petroleum ether). Subsequent recrystallization from mixture of petroleum ether - toluene gave pure compounds.

**1,4-Bis((4-(Octyl(phenyl)amino)phenyl)ethynyl)-9,10-anthraquinone (6a).** Yield 220 mg (25%), mp  $93$ – $95^\circ C$ . IR (neat,  $cm^{-1}$ ): 2949, 2920, 2851 ( $C_8H_{17}$ ), 2176 ( $C\equiv C$ ), 1672 ( $C=O$ ).  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$ : 0.89 (6H, t,  $J$  6.9 Hz, 2Me), 1.30 (20H, m,  $2(CH_2)_5$ ), 1.69 (4H, m,  $2CH_2$ ), 3.72 (4H, t,  $J$  7.8 Hz,  $2NCH_2$ ), 6.81 (4H,

d,  $J$  8.8 Hz,  $H_{Ar}$ ), 7.15 (2H, m,  $H_{Ar}$ ), 7.18 (4H, d,  $J$  7.8 Hz,  $H_{Ar}$ ), 7.37 (4H, d,  $J$  7.8 Hz,  $H_{Ar}$ ), 7.56 (4H, d,  $J$  8.8 Hz,  $H_{Ar}$ ), 7.77 (2H, m,  $H_{Ar}$ ), 7.81 (2H, s,  $H_{Ar}$ ), 8.31 (2H, m,  $H_{Ar}$ ) ppm.  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$ : 14.26, 22.78, 27.18, 27.49, 29.43, 29.53, 31.94, 52.54 ( $2C_8H_{17}$ ), 89.34, 99.23 ( $2C\equiv C$ ), 112.35 (2C), 116.20 (4CH), 123.58 (2C), 124.41 (2CH), 125.50 (4CH), 127.16 (2C), 129.79 (4CH), 133.59 (4CH), 133.68 (2CH), 133.82 (2CH), 133.94 (2C), 138.39 (2CH), 147.00 (2C), 149.02 (2C), 182.02 (2C = O) ppm. HMRS, found:  $[M+H]^+$   $m/z$  814.4472;  $C_{58}H_{58}N_2O_2$   $[M+H]^+$  814.4493.

**1,5-Bis((4-(octyl(phenyl)amino)phenyl)ethynyl)-9,10-anthraquinone (7a).** Yield 290 mg (33%), mp  $124$ – $125^\circ C$ . IR (neat,  $cm^{-1}$ ): 2949, 2920, 2849 ( $C_8H_{17}$ ), 2183 ( $C\equiv C$ ), 1665 ( $C=O$ ).  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$ : 0.88 (6H, t,  $J$  6.9 Hz, 2Me), 1.29 (20H, m,  $2(CH_2)_5$ ), 1.69 (4H, m,  $2CH_2$ ), 3.72 (4H, t,  $J$  7.7 Hz,  $2NCH_2$ ), 6.82 (4H, dt,  $J$  2.5, 8.9 Hz,  $H_{Ar}$ ), 7.15 (6H, m,  $H_{Ar}$ ), 7.37 (4H, m,  $H_{Ar}$ ), 7.55 (4H, dt,  $J$  2.5, 8.9 Hz,  $H_{Ar}$ ), 7.70 (2H, t,  $J$  7.8 Hz,  $H_{Ar}$ ), 7.90 (2H, dd,  $J$  1.3, 7.8 Hz,  $H_{Ar}$ ), 8.31 (2H, dd,  $J$  1.3, 7.8 Hz,  $H_{Ar}$ ) ppm.  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$ : 14.27, 22.79, 27.19, 27.48, 29.44, 29.54, 31.95, 52.54 ( $2C_8H_{17}$ ), 88.43, 97.63 ( $2C\equiv C$ ), 112.40 (2C), 116.35 (4CH), 124.25 (2CH), 124.29 (2CH), 125.35 (4CH), 127.01 (2C), 129.78 (4CH), 132.20 (2C), 132.99 (2CH), 133.49 (4CH), 135.44 (2C), 139.48 (2CH), 147.06 (2C), 148.92 (2C), 181.96 (2C = O) ppm. Found: C, 85.75; H, 6.93; N, 3.39%;  $C_{58}H_{58}N_2O_2$  C, 85.47; H, 7.17; N, 3.44%.

### 3. Synthesis of 2,7-DiR-naphtho[4,3,2,1-lmn] [2,9]phenanthroline and 2,8-DiR-benzo[de]isoquino[1,8-gh]quinoline (general procedure)

#### 3.1. Method A

A mixture of bis(*R*-ethynyl)-9,10-anthraquinone (200 mg, 0.24 mmol), urea (8 g, 133.3 mmol) in DMF (5.5 mL) was refluxed for 14–18 h. A mixture of toluene (50 mL) and water (50 mL) was then added, the organic layer was separated, dried over MgSO<sub>4</sub>, solvent was evaporated in vacuum by rotary. The crude product was purified by column chromatography on alumina (elution with petroleum ether - toluene). Subsequent recrystallization gave pure compounds.

**2,7-Bis(4-(octyl(phenyl)amino)phenyl)naphtho[4,3,2,1-lmn] [2,9]phenanthroline (8a).** Yield 60 mg (31%), mp 164–165 °C (petroleum ether - toluene). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 0.89 (6H, t, *J* 6.9 Hz, 2Me), 1.34 (20H, m, 2(CH<sub>2</sub>)<sub>5</sub>), 1.76 (4H, m, 2CH<sub>2</sub>), 3.81 (4H, t, *J* 7.7 Hz, 2NCH<sub>2</sub>), 7.10 (6H, m, H<sub>Ar</sub>), 7.21 (4H, d, *J* 7.7 Hz, H<sub>Ar</sub>), 7.37 (4H, m, H<sub>Ar</sub>), 7.92 (2H, m, H<sub>Ar</sub>), 8.13 (2H, s, H<sub>Ar</sub>), 8.36 (6H, m, H<sub>Ar</sub>), 9.60 (2H, m, H<sub>Ar</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ: 14.27, 22.81, 27.30, 27.68, 29.49, 29.61, 31.99, 52.63 (2C<sub>8</sub>H<sub>17</sub>), 114.75 (2CH), 116.59 (2C), 118.46 (4CH), 123.10 (2CH), 123.85 (4CH), 125.25 (2C), 128.53 (4CH), 129.21 (2CH), 130.28 (2CH), 131.21 (2C), 133.36 (2C), 136.54 (2C), 146.64 (2C), 147.74 (2C), 149.20 (2C), 153.91 (2C) ppm. Found: C, 85.84; H, 7.24; N, 6.96%; C<sub>58</sub>H<sub>60</sub>N<sub>4</sub> C, 85.67; H, 7.44; N, 6.89%.

**2,8-Bis(4-(octyl(phenyl)amino)phenyl)benzo[de]isoquino[1,8-gh]quinoline (9a).** Yield 75 mg (37%), mp 204–205 °C (petroleum ether - toluene). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 0.89 (6H, t, *J* 6.9 Hz, 2Me), 1.32 (20H, m, 2(CH<sub>2</sub>)<sub>5</sub>), 1.74 (4H, m, 2CH<sub>2</sub>), 3.78 (4H, t, *J* 7.7 Hz, 2NCH<sub>2</sub>), 7.08 (6H, m, H<sub>Ar</sub>), 7.17 (4H, d, *J* 7.7 Hz, H<sub>Ar</sub>), 7.35 (4H, t, *J* 7.5 Hz, H<sub>Ar</sub>), 7.76 (2H, m, H<sub>Ar</sub>), 7.83 (2H, t, *J* 7.5 Hz, H<sub>Ar</sub>), 7.92 (2H, s, H<sub>Ar</sub>), 8.18 (2H, d, *J* 8.7 Hz, H<sub>Ar</sub>), 9.00 (2H, d, *J* 7.7 Hz, H<sub>Ar</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ: 14.25, 22.80, 27.30, 27.67, 29.48, 29.60, 31.98, 52.61 (2C<sub>8</sub>H<sub>17</sub>), 115.02 (2CH), 118.91 (4CH), 122.72 (2CH), 123.32 (4CH), 123.41 (2C), 123.96 (2C), 127.97 (4CH), 128.58 (2CH), 129.58 (4CH), 130.96, (2CH), 131.10 (2C), 132.99 (2C), 137.85 (2C), 147.87 (2C), 148.90 (2C), 150.12 (2C), 151.63 (2C) ppm. Found: C, 85.33; H, 7.09; N, 6.87%; C<sub>58</sub>H<sub>60</sub>N<sub>4</sub> C, 85.67; H, 7.44; N, 6.89%. HMRS, found: [M+H]<sup>+</sup> *m/z* 812.4820C<sub>58</sub>H<sub>60</sub>N<sub>4</sub> [M+H]<sup>+</sup> 812.4813.

#### 3.2. Method B

**2,7-Bis(4-(octyl(phenyl)amino)phenyl)naphtho[4,3,2,1-lmn] [2,9]phenanthroline (8a).** Under argon, a mixture of 1,4-diiodo-9,10-anthraquinone (700 mg, 1.52 mmol), the alkyne **4** (1.4 g, 4.56 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (20 mg, 0.028 mmol), CuI (10 mg, 0.052 mmol) in pyridine (20 mL) was stirred and heated to 60 °C. Then a hot solution of Na<sub>2</sub>CO<sub>3</sub> (550 mg, 5.1 mmol) in H<sub>2</sub>O (8 mL) was added, and the mixture was refluxed for 0.5 h, after toluene (100 mL) was added. The organic layer was separated, was washed with water (3 × 200 mL), dried over MgSO<sub>4</sub> and evaporated to dryness on rotary evaporator. Further urea (25 g, 0.42 mol) and DMF (18 mL) were added, the mixture was refluxed for 18 h. Isolation and purification of compound were analogous to the method A. Yield 265 mg (21.5%), mp 164–165 °C (petroleum ether - toluene).

#### 3.3. Method C

A mixture of diiodo-9,10-anthraquinone (1.4 g, 3.0 mmol) and copper acetylide **5** (1.2 g, 7.0 mmol) in pyridine (25 mL) was stirred under stream of argon at 60–65 °C for 0.5 h. Then ethyl acetate (200 mL) was added, the organic layer was washed with 5% aqueous NH<sub>3</sub> (100 mL) and water (300 mL), dried over MgSO<sub>4</sub> and

evaporated to dryness on rotary evaporator. Further urea (30 g, 0.5 mol) and DMF (21 mL) were added, the mixture was refluxed for 1–3 h. Isolation and purification of compounds were analogous to the method A.

**2,7-Di(thien-2-yl)naphtho[4,3,2,1-lmn] [2,9]phenanthroline (8b).** Yield 350 mg (28%), mp 255–256 °C (toluene). <sup>1</sup>H NMR (DMSO-D<sub>6</sub>, 400 MHz) δ: 7.24 (2H, dd, *J* 3.6, 5.1 Hz, H<sub>Ar</sub>), 7.52 (2H, dd, *J* 1.2, 5.1 Hz, H<sub>Ar</sub>), 7.90 (2H, dd, *J* 1.2, 3.6 Hz, H<sub>Ar</sub>), 7.94 (2H, m, H<sub>Ar</sub>), 8.07 (2H, d, *J* 1.5 Hz, H<sub>Ar</sub>), 8.24 (2H, d, *J* 1.5 Hz, H<sub>Ar</sub>), 9.48 (2H, m, H<sub>Ar</sub>) ppm. <sup>13</sup>C NMR (DMSO-D<sub>6</sub>, 100 MHz) δ: 114.75 (2CH), 116.14 (2C), 124.65 (2CH), 126.05 (2CH), 128.87 (2CH), 129.23 (2CH), 129.98 (2CH), 130.86 (2CH), 132.00 (2C), 136.50 (2C), 145.20 (2C), 145.47 (2C), 149.34 (2C) ppm. Found: C, 74.78; H, 3.30; N, 6.70; S, 15.47%; C<sub>26</sub>H<sub>14</sub>N<sub>2</sub>S<sub>2</sub> C, 74.61; H, 3.37; N, 6.69; S, 15.32%.

**2,8-Di(thien-2-yl)benzo[de]isoquino[1,8-gh]quinoline (9b).** Yield 420 mg (34%), mp 329–330 °C (pyridine). <sup>1</sup>H NMR (DMSO-D<sub>6</sub>, 400 MHz) δ: 7.27 (2H, dd, *J* 3.6, 5.0 Hz, H<sub>Ar</sub>), 7.73 (2H, dd, *J* 1.0, 5.1 Hz, H<sub>Ar</sub>), 7.99 (4H, m, H<sub>Ar</sub>), 8.09 (2H, d, *J* 7.8 Hz, H<sub>Ar</sub>), 8.37 (2H, s, H<sub>Ar</sub>), 8.86 (2H, dd, *J* 0.9, 7.2 Hz, H<sub>Ar</sub>) ppm. Found: C, 74.38; H, 3.37; N, 6.73; S, 15.21%; C<sub>26</sub>H<sub>14</sub>N<sub>2</sub>S<sub>2</sub> C, 74.61; H, 3.37; N, 6.69; S, 15.32%.

#### 3.4. X-ray crystal structure analysis for compound 8b

Formula: C<sub>26</sub>H<sub>14</sub>N<sub>2</sub>S<sub>2</sub>, *M<sub>r</sub>* = 418.51, yellow crystal, monoclinic, space group; *P*<sub>2</sub><sub>1</sub>/*c*, *a* = 12.0189 (6), *b* = 7.7609 (4), *c* = 21.7992 (11) Å, β = 105.817 (2)°, *V* = 1956.38 (17) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.421 g/cm<sup>3</sup>, μ = 0.288 mm<sup>-1</sup>, crystal size 0.02 × 0.08 × 0.58 mm<sup>3</sup>, 4729 independent reflections were collected, *wR*<sub>2</sub> = 0.1675, *S* = 1.06 for all reflections, the final *R* index was 0.0507 for 3426 *F* > 4σ).

#### 3.5. X-ray crystal structure analysis for compound 9b

Formula: C<sub>26</sub>H<sub>14</sub>N<sub>2</sub>S<sub>2</sub>, *M<sub>r</sub>* = 418.51, red crystal, orthorhombic, space group, *Pbca*, *a* = 17.3336 (5), *b* = 10.7758 (4), *c* = 20.3308 (7) Å, *V* = 3797.5 (2) Å<sup>3</sup>, *Z* = 8, *D<sub>c</sub>* = 1.464 g/cm<sup>3</sup>, μ = 0.297 mm<sup>-1</sup>, crystal size 0.06 × 0.18 × 0.41 mm<sup>3</sup>, 4447 independent reflections were collected, *wR*<sub>2</sub> = 0.1639, *S* = 1.06 for all reflections, the final *R* index was 0.0482 for 3378 *F* > 4σ).

CCDC 1475062 (**8b**) and 1475063 (**9b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## 4. Results and discussion

### 4.1. Synthesis and characterization

The synthetic route for the diazabenzopyrenes **8** and diazaperenylenes **9** is illustrated in Scheme 1. The alkyne **4** was synthesized in several steps from diphenylamine. Initially alkylation of diphenylamine with 1-bromooctane in aqueous NaOH solution in the presence of the BTEAC at reflux led to *N*-octyldiphenylamine **1** with 87% yield. 4-Iodo-*N*-octyldiphenylamine **2** was synthesized with 52% yield by iodination of compound **1** with I<sub>2</sub> in aqueous KHCO<sub>3</sub> solution. Then, the iodide **2** was subjected by Sonogashira reaction with 1-ethynylcyclopentanol to obtain the alkynol **3** (yield 92%). The alkynol **3** was cleaved with alkali in toluene under reflux to the alkyne **4** with 83% yield. Copper acetylide **5** was produced from 2-ethynylthiophene and CuCl in aqueous solutions of NH<sub>3</sub>, NH<sub>4</sub>Cl, and NH<sub>2</sub>OH·HCl with 94% yield. These conditions were not suitable for preparation of copper acetylide from alkyne **4**. For this reason, for the synthesis of bis(*R*-ethynyl)-9,10-anthraquinones **6a**, **7a** the Sonogashira coupling reaction was used. The bis(*R*-ethynyl)-9,10-anthraquinones **6b**, **7b** was synthesized by Castro–Stephens coupling reaction. Synthesis of polycondensed compounds **8**, **9** was

based on heterocyclization of bis(*R*-ethynyl)-9,10-anthraquinones with urea similar to that previously reported by us [28,29]. That method allows using crude alkyne therefore the stages of cross-coupling and heterocyclization are advisable to be carried out in a one-pot. The crude bis-alkyne **6a** without purification after Sonogashira coupling was cyclized to compound **8a** (method B). Compounds **8b** and **9b** were prepared via cyclization of the corresponding crude alkynes **6b** and **7b** after Castro–Stephens coupling (Method C). It has been found that using *R* substituents with strong donor properties decreases electrophilicity of reaction centers (C=O, C≡C), which results in deactivation of the bis-alkyne **6, 7** in the reaction with a nucleophile (urea). For example, the time of cyclization of bis-alkynes **6a, 7a** containing 4-(phenylamino) phenyl substituents was significantly higher (19 h) than in the case of anthraquinones with propargyl and alkynyl substituents (0.5–2 h). The compounds were characterized by elemental analysis, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectrometry. Crystals of heterocycles **8b, 9b** we investigated by X-ray analysis.

#### 4.2. Molecular structure and crystal packing of **8b** and **9b**

Crystals of **8b** suitable for X-ray diffraction analysis were obtained by solvent evaporation from toluene solution. Under these conditions compound **8b** crystallized in centrosymmetrical P2<sub>1</sub>/c space group in a monoclinic system, with four molecules in one crystallographic unit cell (Fig. 1). Compound **8b** is asymmetrical with one thiophene ring reverted out of phenanthroline plane by 13°. Also **8b** forms  $\pi$ -stacked layers consisted of face-to-face dimers with  $\pi$ - $\pi$  dimer distance 3.382 Å and interdimer distance 3.427 Å following a “herringbone” packing of neighboring layers. Two molecules in each dimer overlap through main conjugation backbone of the molecule.

The molecules of **9b** were packed with orthorhombic *Pbca* symmetry in a “herringbone” layered structure (Fig. 2d). Both thiophene rings are twisted about ~5° to diazaperylene unit. In

contrast to **8b** no  $\pi$ - $\pi$  stacked dimers were observed but only separated dimers (Fig. 2b). These  $\pi$ - $\pi$  dimers have 3.544 Å interplanar distance (Fig. 2d). The dimers are shifted respectively each other so that the intercentroid distance between thiophene ring of one dimer and benzene ring of diazaperylene core of another dimer is 3.926 Å (Fig. 2c).

#### 4.3. Theoretical calculations

Quantum chemical calculations were used for theoretical study of frontier orbitals. For compounds **8a** and **9a** the long octyl chain was replaced by methyl group (compounds **8a\*** and **9a\***) to simplify the calculations and reduce influence of conformers. According to calculations the torsion angle between benzene ring and heteroaromatic unit in **8a\*** and **9a\*** was found approximately 22° and both molecules **8b** and **9b** were found to be completely flat. The frontier molecular orbitals and their energy levels obtained by DFT calculations are shown in Fig. 3 and Table S1. As can be seen from Fig. 3 for all substrates LUMO is mainly delocalized on the electron deficient polycyclic heteroaromatic central unit and HOMO is delocalized along the main conjugation chain of the molecule.

#### 4.4. Spectroscopic and electrochemical properties

For the synthesized molecules the energy levels of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and HOMO–LUMO gaps ( $E_g$  or  $E_g^{opt}$ ) were obtained from cyclic-voltammetry (CVA) experiments and from UV–vis absorption and luminescence emission spectra (Table 1).

CVA revealed reversible oxidation peaks for **8a** whereas other compounds demonstrate irreversible and quasi-reversible oxidation peaks (Fig. 4). The irreversibility of the oxidation peaks of thieryl-capped molecules (**8b** and **9b**) could be due to the oxidative electropolymerization processes which was demonstrated for thiophene containing compounds [39]. Reduction peaks were also

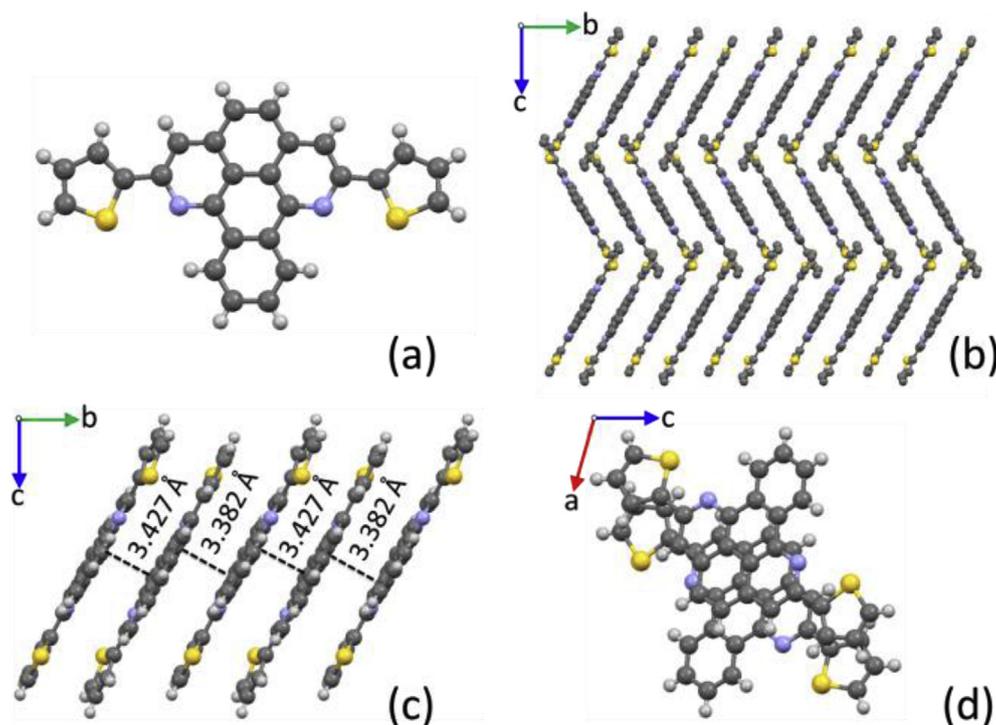
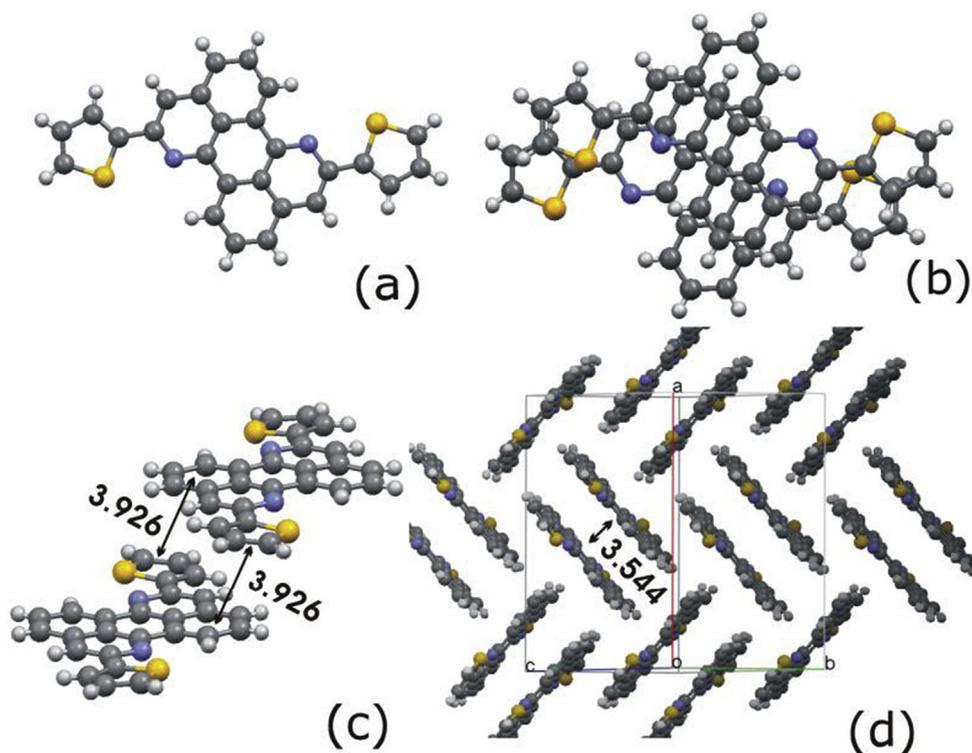
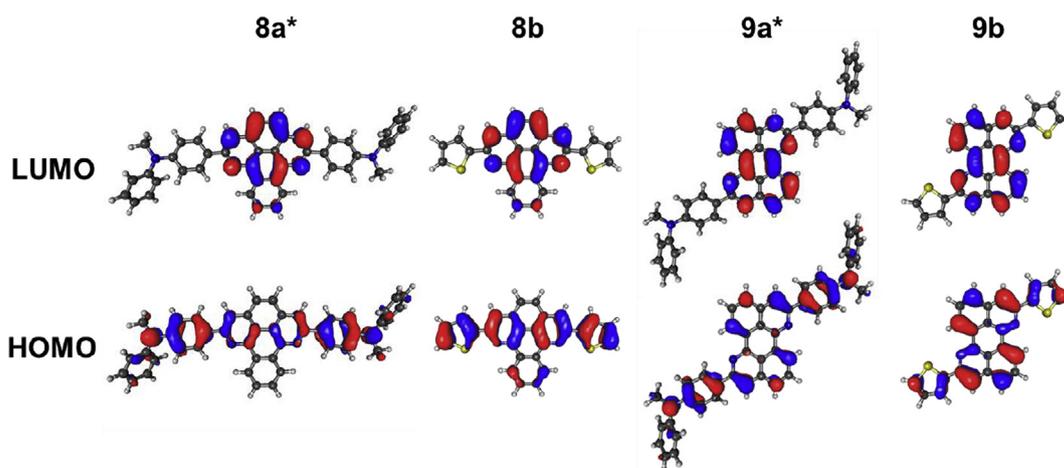


Fig. 1. Crystallographic data of compound **8b**: the single-molecule (a), herring-bone packing in the crystal (b),  $\pi$ - $\pi$  interdimer distances (c), and the stacked dimers along *b*-axis (d).



**Fig. 2.** Crystallographic data of compound **9b**: the single-molecule (a), the  $\pi$ - $\pi$  stacked dimer (b), the slippage/shift of dimers (c), herring-bone packing in the crystal, view along  $b + c$  (d).



**Fig. 3.** HOMO, and LUMO orbitals for **8a\***, **8b** and **9a\***, **9b** with a 0.03 isocontour value.

**Table 1**  
Spectroscopic and electrochemical properties of compounds **8**, **9** in solution.

Compound	$E_{\text{HOMO}}^a$ , eV	$E_{\text{LUMO}}^a$ , eV	$E_g^a$ , eV	$E_g^{\text{optb}}$ , eV	$\lambda_{\text{max}}^{\text{abs}}$ , nm (solution)	$\lambda_{\text{max}}^{\text{em}}$ , nm (solution)	$\lambda_{\text{max}}^{\text{em}}$ , nm (solid)	$\epsilon$ , $10^3 \text{ M}^{-1}\text{cm}^{-1}$ ( $\lambda$ , nm) <sup>c</sup>	$\phi^d$
8a	-5.12	-2.76	2.36	2.74	384	491	543	74 (384)	0.10
8b	-5.52	-2.84	2.68	2.82	346, 435	443	557	4.6 (435)	0.08
9a	-5.12	-3.07	2.05	2.41	351, 478	561	600	29 (450)	0.15
9b	-5.72	-3.22	2.50	2.57	315, 477	489	660	31 (477)	0.5

<sup>a</sup> Energies measured by CVA.

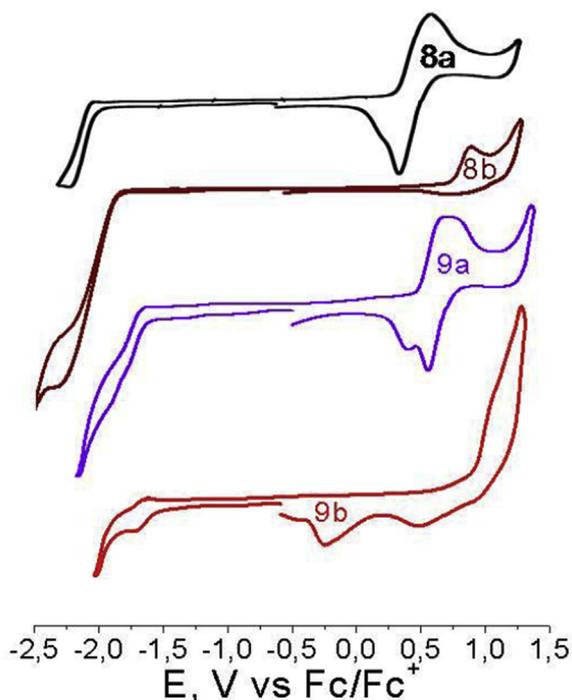
<sup>b</sup>  $E_g^{\text{opt}}$  estimated from the intersection point of UV–vis absorption spectrum and luminescence emission spectrum in toluene.

<sup>c</sup> Extinction coefficients  $\epsilon$  (at wavelengths which are specified in the brackets).

<sup>d</sup> Luminescence quantum yields  $\phi$  in toluene solutions.

observed for all compounds, and the LUMO levels was estimated from reduction potentials correspondingly (Table 1).

For the toluene solutions of compounds **8** and **9** UV–vis absorption spectra and luminescence emission spectra are presented



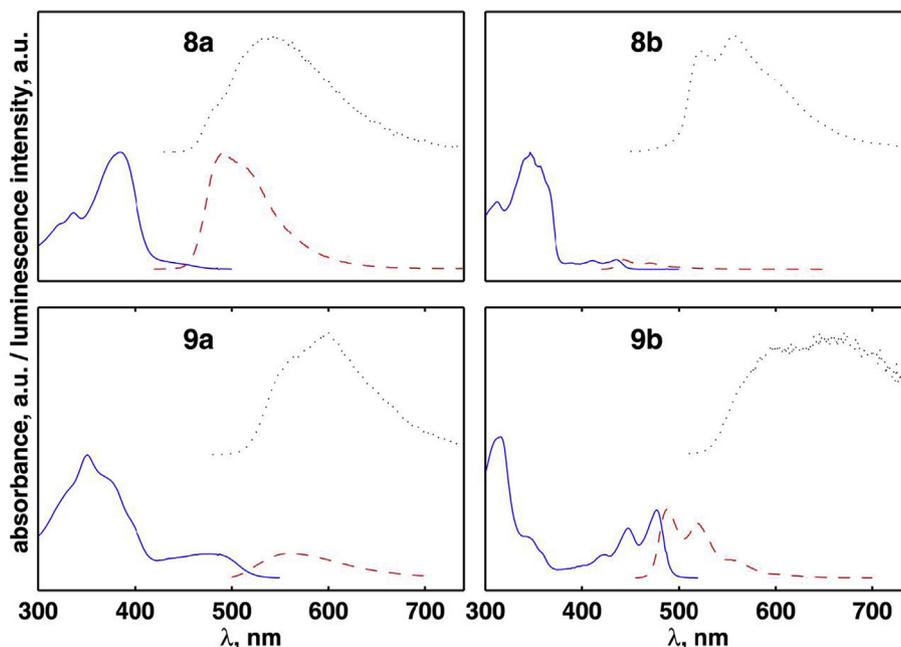
**Fig. 4.** Cyclic voltammetry plots of compounds **8**, **9** measured in  $\text{CH}_2\text{Cl}_2$  solution. Potentials calibrated vs  $\text{Fc}/\text{Fc}^+$  as an internal standard.

in Fig. 5. The HOMO-LUMO gaps were obtained from the intersection points of UV-vis absorption spectra and luminescence emission spectra as it was found from Fig. 5. The characteristic values of molar absorption coefficients  $\epsilon$  and luminescence quantum yields  $\phi$  for the investigated substances in toluene are presented in Table 1. The non-substituted 1,7-diazaperylene has almost unity fluorescence quantum yield  $\phi$  [40], however substitution of 1,7-diazaperylene at 2,8-positions results in decrease of  $\phi$  value.

The optical and electrochemical properties which have been obtained for substances **6–9** are available in Table S1, Supplementary Data. From the comparison of the HOMO-LUMO gaps and the absorption coefficients of 1,8-diazabenzopyrenes **8** and 1,7-diazaperylenes **9** we can observe that the 4-(phenylamino)phenyl groups not only decrease the HOMO-LUMO gaps but also increase the absorption coefficients. A similar effect is produced by thienyl and phenyl [29] substituents but its strength is smaller (see Table S1, Supplementary Data). This effect could be caused by expansion of  $\pi$ -conjugation to the aromatic substituents with electron donor properties.

The UV-vis and luminescence spectra of **8** and **9** in toluene have very similar lineshape to those obtained in pure dioxane solution (Fig. S3, Supplementary Data) but luminescence spectra of drop-casted films are shifted into the red region (Fig. 5).

In order to observe and discuss possible changes in the intensities and lineshapes of UV-vis and luminescence spectra in conditions when solid-state aggregates are appearing, the spectra of **8** and **9** at mixtures of water and dioxane were measured with different water concentrations (Fig. S3, Supplementary Data). The luminescence bands of **8** and **9** in solid states and in dioxane/water mixtures at high water concentrations revealed close similarity. The substances **8** and **9** have low solubility in water and aggregates of the molecules are expected in dioxane/water mixtures, so at these mixtures the solid-state luminescence is probably observed. The similar approach was presented in the works [41,42] to observe solid-state luminescence of diazabenzopyrenes and benzantrones in solutions. The solid-state origin of luminescence of **8b** and **9b** in dioxane/water solutions was confirmed by the luminescence lifetimes of **8b** and **9b** which were obtained very similar for the solid states and the dioxane/water mixtures at high water concentrations (Fig. S4 and Table S2 in Supplementary Data). In contrast, the luminescence lifetimes of **8b** and **9b** in net dioxane strongly differ from those in the solid states (Fig. S4 and Table S2 in Supplementary Data) which reveal the difference in origins of luminescence bands of **8b** and **9b** in solutions (in toluene or net dioxane) and in solid state (Fig. S4, Supplementary Data).



**Fig. 5.** UV-vis absorption spectra (solid lines) and luminescence emission spectra of the compounds **8** and **9** in toluene (dash lines), of drop-casted films (dot lines). The spectra were normalized to match the intensity of long-wavelength maximum of absorption and short-wavelength maximum of luminescence spectra.

## 5. Conclusions

A simple and effective one-pot synthetic route was applied to obtain diaza-analogs of benzopyrene and perylene containing thienyl and 4-(phenylamino)phenyl groups. The method which demonstrated broad synthetic capabilities was tested in the preparation of polycondensed molecules with substituents of different types (aliphatic, aromatic, heteroaromatic). For the preparation of compounds with the desired substituents it is sufficient to use the appropriate terminal alkyne on the stage of cross-coupling with diiodoanthraquinone. The 1,8-diazabenzopyrenes **8** and 1,7-diazaperylenes **9** are convenient building blocks, which can be used in the synthesis of the new small molecules, oligomers and copolymers. The strongest effect was revealed when two diphenylamine substituents were bonded to the cores: decreasing of HOMO-LUMO gaps and luminescence yields, and increasing of extinction coefficients were observed. The solid-state luminescence was obtained for the synthesized substances in drop-casted films and in solutions of dioxane and water mixtures. The obtained electrochemical, optical and luminescent properties of new substances show possibility for their applications as building units for semiconducting materials in organic electronics, and optical or luminescence sensing devices.

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## Appendix B. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.dyepig.2016.09.026>.

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