Synthesis and Properties of Substituted *p*-Phenylenediamine Donor and 1*H*-indene-1,3(2*H*)-dione Acceptor-Based Chromophores

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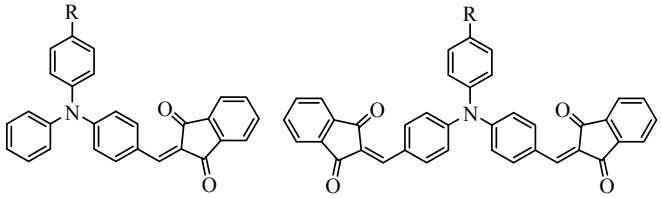
Abstract. **In order to evaluate the influence of insertion of the strong electron-donating groups on the *p*-position of triphenylamine unit upon physical properties novel chromophores containing *N,N*-dibutyl- or *N,N*-diphenylsubstituted triphenylamine donor and 1*H*-indan-1,3(2*H*)-dione acceptor have been synthesized *via* Knoevenagel condensation reaction of 4-((4-dibutylamino)phenyl) (phenyl)amino)benzaldehyde, 4,4'-(4-(dibutylamino) phenylazanediyl)dibenzaldehyde and 4,4'-(4-diphenylamino) phenylazanediyl) dibenzaldehyde with 1*H*-indan-1,3(2*H*)-dione. Vilsmeier-Haack formylation reaction of 4-bromo-*N,N*-diphenylbenzenamine and N^1,N^1-dibutyl-N^4,N^4-diphenylbenzene-1,4-diamine has been examined. It is shown that direct twofold Vilsmeier-Haack formylation of N^1,N^1-dibutyl-N^4,N^4-diphenylbenzene-1,4-diamine to get 4,4'-(4-(dibutylamino) phenylazanediyl)dibenzaldehyde with satisfactory yield is not possible but it could be obtained from 4,4'-(4-bromphenylazanediyl)dibenzaldehyde in a two-step process: first, protection of carbonyl groups, then Pd catalyzed amination followed by deprotection. 4,4'-(4-Diphenylamino) phenylazanediyl)dibenzaldehyde has been obtained in double *N*-arylation of N^1,N^1-diphenylbenzene-1,4-diamine with 2-(4-bromophenyl)-4-methyl-1,3-dioxolane under palladium(0) catalysis. All obtained chromophores have good solubility in common organic solvents. Thermal properties are little influenced by insertion of diphenylamino substituent, but substantially by dibutylamino substituent in the parent structure. Negative solvatochromism and slight bathochromic shift of charge transfer band of novel chromophores compared with unsubstituted triphenylamine core containing chromophores are observed in UV-Vis spectra. Chromophores containing two tertiary amine moieties in the molecule undergo irreversible anodic oxidation, and influence of substituents on the oxidation potentials has been studied. Nitrogen *N*-4 is shown as the primary reaction centre in the anodic oxidation. The cathodic reduction of the studied compounds proceeds close to -1 V. The reduction potentials of the electron acceptor 1*H*-indene-1,3(2*H*)-dione moieties are less sensitive to the substituent effects in the molecules.**

Keywords. **chromophores, triphenylamine**

I. Introduction

The molecule triphenylamine (TPA) and derivatives thereof are applied as hole-transport materials in electrophotography, and in organic light emitting diodes. They are used in the backbone or in side-groups of polymers applied in light emitting diodes. Star-shaped oligomers and dendrimeric structures of TPA are attractive photo- and electro-active organic materials because of theirs amorphous nature [1]. The Large number of D-π-A type chromophores with TPA and its derivatives as donors has been developed. They were obtained from mono-, di-, and tri-aldehydes of TPA employing Knoevenagel condensation[2], Wittig[3,4] and Horner-Wadsworth-Ermons reactions[5], as well as from halogen derivatives of TPA [6-8] and by arylation of diphenylamine[9-13].

Recently synthesis of D-π-A type chromophores **1a** and **2a** was reported by condensation of aldehydes of TPA with indan-1,3-dione[14]. The latter was chosen because of its electron withdrawing strength as the acceptor and its ability to produce chromophores with impressive optical nonlinearity. The aim of this research was to obtain new chromophores **1b** and **2b, 2c** and to evaluate the influence of insertion of the strong electron-donating dibutylamino or diphenylamino substituent on the *p*-position of TPA unit upon physical properties of chromophores.



1a, **b** **2a-c**

R=H (**a**); NBu_2 (**b**) R=H (**a**); NBu_2 (**b**); NPh_2 (**c**)

II. Results and Discussion

As a starting material for chromophores **1b** and **2b,** 4-bromo-*N,N*-diphenylbenzenamine (**4**) has been chosen. Previously compound **4** with 78 – 90% yield was obtained in the reaction of triphenylamine (**3**) with equimolar amount of NBS and was purified by recrystallization[15-17]. Repeating several times these experiments, reported results were not reproduced. Under various conditions formation of byproduct 4,4'-dibromotriphenylamine with very similar to compound **4** solubility and R_f was observed. Thus, chromophores **1b** and **2b** were synthesized using compound **4** in admixture with 4,4'-dibromotriphenylamine ~10% and compound **3** ~10% that were separated by column chromatography after the next amination and formylation stages.

An effective route to chromophore **1b** is a four-step synthesis (Fig. 1). Amination of compound **4** with di-*n*-butylamine, using standard Buchwald-Hartwig reaction conditions: $Pd(OAc)_2$/BINAP catalyst system in the presence of KO_tBu as a base, led to previously unknown N^1,N^1-dibutyl-

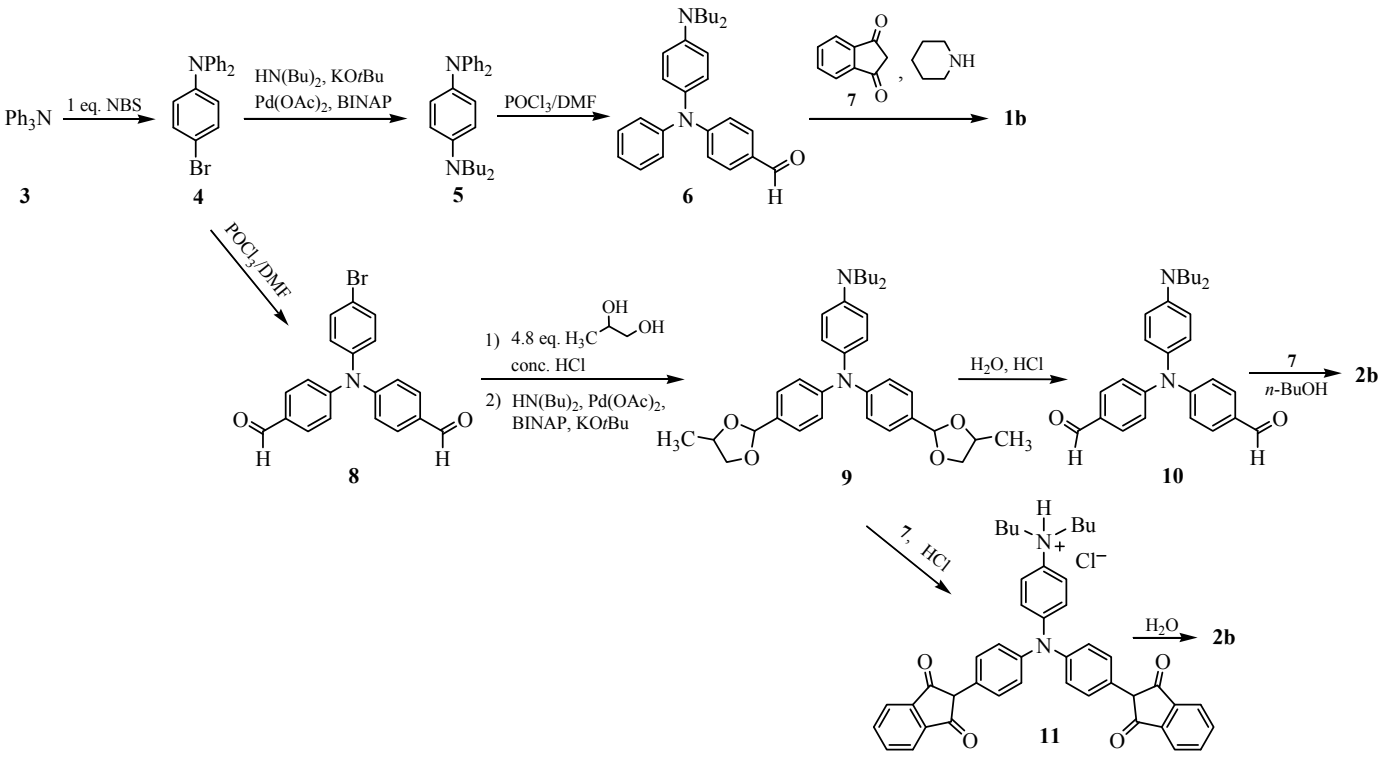
N^4,N^4-diphenylbenzene-1,4-diamine (**5**), the brownish oil, turning blue in the air, especially being in the solution of CH_2Cl_2 or in silica gel. Although the structure of this blue material was not determined, it was presumed to be radical cation with a similar structure to the so-called Wurster's blue – forming in oxidation of N^1,N^1,N^4,N^4-tetramethylbenzene-1,4-diamine[18].

In order to obtain 4-((4-dibutylamino)phenyl)(phenyl) amino)benzaldehyde (**6**) formylation of diamine **5** has been investigated. It was reported in the literature that Vilsmeier-Haack formylation of compound **3** using a single equivalent of $POCl_3$ afforded 4-diphenylaminobenzaldehyde in 94% yield, but a large excess (25 eq.) of $POCl_3$ – diformyltriphenylamine in 81% yield[19,20]. Supposing that introduction of dibutylaminogroup in compound **3** would activate benzene ring towards formylation, 1 eq of $POCl_3$ was applied; however, consumption of starting diamine **5** required 24 h of heating to 80º C and yield of compound **6** was only 40%. Besides, formation of large amount of byproducts was observed. Screening Vilsmeier-Haack formylation conditions it was found out that monoaldehyde **6** could be synthesized from diamine **5** with 60% yield using 2 eq. $POCl_3$ and 2.16 eq. DMF, and optimal reaction time was 3 h heating to 80º C. Condensation of aldehyde **6** with 1*H*-indene-1.3(2*H*)-dione (**7**) in the presence of catalytic amounts of piperidine led to chromophore **1b**.

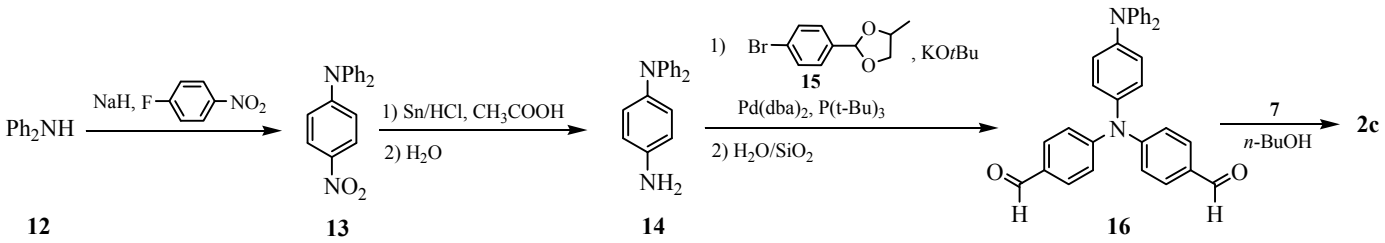
Direct twofold Vilsmeier-Haack formylation of compound **5** to synthesize 4,4'-(4-(dibutylamino)phenylazanediyl) dibenzaldehyde (**10**) that was precursor for chromophore **2b** proved to be unsuccessful: applying 25 eq. $POCl_3$ and 23 eq. DMF, 20 hours of heating were necessary for consumption of all starting compounds; intractable tars were the main product; dialdehyde **10** yield was only 17%. Therefore compound **10** was obtained in a two-step process. Formylation of compound **4** using 25 eq. $POCl_3$ and 23 eq. DMF and 7 hours of heating gave 4,4'-(4-bromphenylazanediyl)dibenzaldehyde (**8**) in 55% yield and as byproduct 4-((4-bromphenyl)(phenyl) amino)benzaldehyde in 21% yield. Before Pd catalyzed amination formyl groups of obtained dialdehyde were protected refluxing compound **8** in benzene for seven days with 4.8 eq. of propan-1,2-diole and conc. HCl as catalyst.

N^1,N^1-Dibutyl-N^4,N^4-bis(4-(4-methyl-1,3-dioxolan-2-yl) phenyl)benzene-1,4-diamine (**9**) was obtained in 60% yield from protected compound **8** and dibutylamine using the same catalyst system as for obtaining diamine **5**. It was noted that significantly the yield of diamine **9** was determined, when starting material did not contain partly unprotected aldehyde, otherwise reaction yield was low. Compound **9** was then deprotected under very mild conditions – at room temperature in MTBE in argon atmosphere using small excess of conc. HCl. Knoevenagel condensation of dialdehyde **10** with diketone **7** by refluxing in *n*-butanol yielded chromophore **2b**. Alternatively chromophore **2b** could be synthesized without deprotection step – from compounds **9** and **7** in *n*-butanol by adding to the solution small excess of conc. HCl and boiling the mixture for 1½ h. Salt **11** precipitated, which after hydrolysis gave chromophore **2b**.

Synthesis of 2,2'-(4,4'-(4-(diphenylamino)phenyl-azanediyl)bis(4,1-phenylene)bis(methanylidene)bis(1H-indene -1,3(2H)-dione) (**2c**) is presented in the Scheme 2.



Scheme 1



Scheme 2

At first, sodium derivative of diphenylamine (**12**) was *N*-arylated with 1-fluoro-4-nitrobenzene in DMF to yield 4.4-nitro-*N,N*-diphenylaniline (**13**). Reduction of the nitro group according to procedure[21] by using tin in acetic acid gave instead of N^1,N^1-diphenylbenzene-1,4-diamine (**14**), as reported, its N^4-acetylderivative and only after boiling reaction product for 2 days with aqua HCl desired amine **14** was obtained. Double *N*-arylation of amine **14** with 2-(4-bromophenyl)-4-methyl-1,3-dioxolane (**15**) under palladium(0) catalysis, using tri-*terc*-butilphosphine as ligand and NaO*t*Bu as a base gave N^1,N^1-bis(4-(4-methyl-1,3-dioxolan-2-yl)phenyl)-N^4,N^4-diphenylbenzene-1,4-diamine containing mixture, that after dissolution in CH_2Cl_2 was subjected to column chromatography on SiO_2. During chromatography deprotecton of formyl groups proceeded and 4,4'-(4-diphenylamino)phenylazanediyl)dibenzaldehyde (**16**) was obtained**.**

Knoevenagel condensation of dialdehyde **16** with compound **7** in boiling n-butanol yielded chromophore **2c** in 94% yield.

All obtained chromophores have good solubility in common organic solvents, such as dichloromethane, chloroform, THF, toluene at room temperature. Their behaviour upon heating was determined by differential scanning calorimetry (DSC) and thermogravimetry (TGA) measurements. Melting points (T_m) and decomposition temperatures (T_{onset}) of compounds **1b** and **2a-c** are listed in Table 1.

Chromophore **2a** shows relatively high melting point (261ºC) and thermal stability – up to about 390 ºC. Thermal properties are little influenced by insertion of diphenylamino-substituent in its structure – T_m and T_{onset} of compound **2c** are 250 and 370 ºC, respectively. On the contrary, existence of aliphatic dibutylamino segment in the structure (compound **1b** and **2b**) substantially lowers the melting point and the decomposition temperature. The glass transition temperature of **1b** and **2b** was observed at 146 and 82 ºC, but decomposition temperature at 262 and 234 ºC, respectively.

TABLE 1

The thermal properties of compounds **1b**, **2a-c**

Compound	T_m, ºC	T_{onset}, ºC
1b	146.3	262.24
2a	261.5	394.33
2b	81.97	235.94
2c	250.09	373.89

The *UV-Vis* spectra of all chromophores were taken in toluene and acetonitrile and are shown in Table 2. Chromophores containing one acceptor group **1a** and **1b** show in *UV-Vis* spectra in toluene two absorption maxima at 295, 484, and 376, 506 nm, respectively. These absorption bands can be attributed – the first to local $\pi \rightarrow \pi^*$ transitions, the second to the intramolecular charge transfer between the triphenylamine donor core and the 1*H*-indene-1,3(2*H*)-dione acceptor group. Chromophores containing two acceptor groups have in toluene three absorption maxima, the first arising from local $\pi \rightarrow \pi^*$ transitions, remaining from charge transfer transitions, so chromophore absorb: **2a** – at 296 nm, 435 nm, 517 nm, chromophore **2b** - at 340 nm, 397 nm, 545 nm, chromophore **2c** – at 308 nm, 460 nm, 531 nm. Table 2 shows that absorption bands of chromophores in acetonitrile are slightly blue-shifted (≤13 nm) compared with that in toluene, so negative solvatochromism is observed.

TABLE 2

UV-vis spectra of chromophores

Com-pound	*UV-Vis* toluene λ_{max}, nm(lgε)	*UV-Vis* acetonitrile λ_{max}, nm (lgε)	$\Delta\lambda_{max}$ (toluene-acetonitrile)*, nm
1a	295 (4.58) 484 (5.04)	288 (4.35) 478 (4.80)	 6
1b	376 (3.95) 506 (4.55)	384 (3.83) 493 (4.56)	 13
2a	296 (4.30) 435 (4.34) 517 (4.77)	300 (4.43) 431 (4.45) 510 (4.85)	 7
2b	340 (3.95) 397 (3.84) 545 (4.4)	334 (4.29) - 536 (4.68)	- 9
2c	308 (4.62) 460 (4.50) 531 (4.81)	304 (4.33) 440 (4.24) 524 (4.60)	4 20 7

* charge-transfer bands

Incorporation of dibutylamino or diphenylamino group in triphenylamine core causes slight bathochromic shift of charge transfer band of these chromophores compared with unsubstituted triphenylamine core containing chromophores, so chromophores **1b**, **2b**, **2c** absorb in the longer wave region compared with **1a**, **2a**. This can be attributed to stronger electron-donor ability of N^1,N^1-dibutyl-N^4,N^4-diphenyl-*p*-phenylenediamine and N^1,N^1-diphenyl-N^4,N^4-diphenyl-*p*-phenylenediamine than that of triphenylamine. Chromophores **2a**, **2b**, **2c**, which contain two 1*H*-indene-1,3(2*H*)-dione fragments, absorb in the longer wave region compared to monosubstituted analogue **1a**, **1b**.

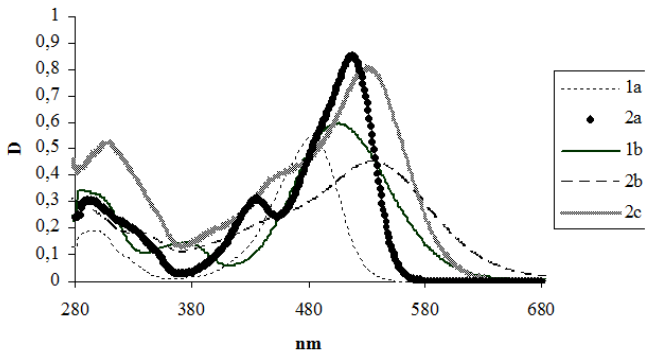


Fig. 1 UV-vis spectra of chromophores in toluene

The luminescence spectra of all chromophores were taken in dichloromethane solutions. To evaluate the relative intensity of emission, solutions of chromophores with equal long wave absorption band optical densities were used and 2-(4-*N*,*N*-dimethylaminobenzylidene)indan-1,3-dione (DMABI) was taken as a standard. Chromophore **2a** has the strongest luminescence: initiate at 521 nm, it emits at 600 nm and emission intensity is 26 times stronger compared with DMABI, while chromophore **2b** has very weak luminescence – initiate at 538 nm, it emits at 622 nm. Chromophores **1b**, **2c** do not luminesce.

The synthesized compounds are interesting objects for electrochemical investigations. As charge transfer complexes they could be investigated on the one hand by anodic oxidation, on the other – by catodic reduction.

In the literature electrochemical oxidation of triphenylamine derivatives has been studied in detail[22,23]. Triphenylamines with the blocked *p*-positions undergo reversible anodic oxidation producing stable cation radicals in acetonitrile. These compounds are widely studied as they could be applied as charge transfer mediators to the indirect electrochemical oxidation. The advantage of triphenylamines is the possibility of varying their oxidation potentials over a wide range by proper selection of the *ortho*- and *para*- substituents. For example, in acetonitrile tri-*p*-tolylamine undergoes reversible electrochemical oxidation at 0.77 V (Fig. 2 b).

Substitution of *p*-positions of triphenylamine by two strong electron acceptors 1*H*-indene-1,3(2*H*)-dione moieties (compound **2a)** and probably due the sterical hindrance for the nitrogen of the amine, shifts its oxidation potential behind 2.7 V – the usable potential range (Fig. 2a).

At the same time, compounds **1b**, **2b** and **2c** containing two tertiary amine moieties in the molecule undergo irreversible anodic oxidation (Fig. 3), so one can conclude that the first electron is lost from the nitrogen of the amine, which is distanced from the electron-acceptor groups and therefore is less sterically hindered. In acetonitrile compound **2c** undergoes irreversible oxidation at 0.91 V, which is in agreement with the 1e irreversible oxidation of triphenylamine at 0.92 V given in the literature[24]. To check the reaction centre the influence of substituents on the oxidation potentials (Table 3) was studied, too.

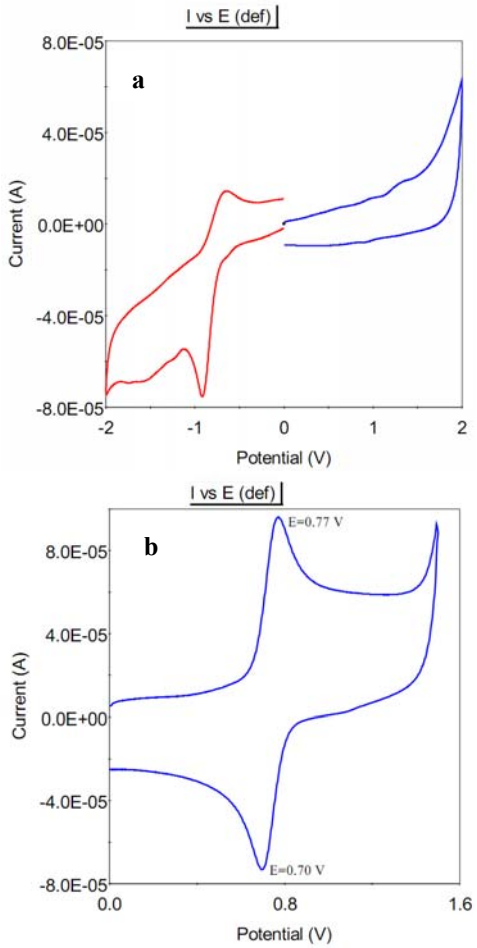


Fig. 2. Cyclic voltammograms registered in 0.1 M $TBAPF_6$ / MeCN solution **a** tri-*p*-tolylamine (c = $5x10^{-4}$ M).;**b** compound **2a** (c = saturated)

Presence of two electron-donating butyl groups in the dibutylamino moiety of compound **2b** relieves the anodic process for ΔE_{ox} = 330 mV comparing with the compound **2c** bearing two weak electron-acceptor phenyl groups in the diphenylamino moiety. Presence of one (compound **1b**) or two (compound **2b**) strong electron acceptors 1*H*-indene-1,3(2*H*)-dione moieties has much less influence (ΔE_{ox} = 50 mV) on the oxidation potentials. Substituent effects confirmed that the nitrogen *N*-4 is the primary reaction centre in the anodic oxidation of compounds **1b**, **2b**, **2c**. Contrary to the oxidation of tri-*p*-tolylamine, the first intermediate is unstable radical cation. It has been shown[25] that triphenylamines are oxidized to tetraphenylbenzidines, which may be reversibly oxidized to their dications.

The reduction potentials of the electron acceptor 1*H*-indene-1,3(2*H*)-dione moieties are less sensitive to the substituent effects in the molecules. The catodic reduction of the studied compounds proceeds close to -1 V (Table 3). Anion radical – the primary product of the electrochemical reduction is unstable in all cases, so the transfer of the first electron is followed by fast chemical reaction.

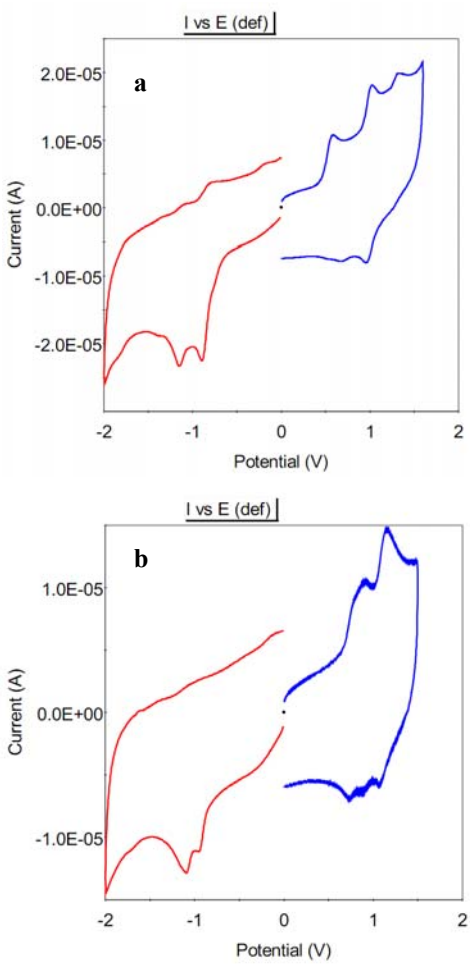


Fig. 3. Cyclic voltammograms registered in 0.1 M $TBAPF_6$ / MeCN solution **a** compound **2b** (c = saturated); **b** compound **2c** (c = saturated)

TABLE 3

POTENTIALS OF ELECTROCHEMICAL REDOX REACTIONS OF THE COMPOUNDS IN 0.1M $TBAPF_6$/MECN SOLUTION ON GLASSY CARBON ELECTRODE.

Compound	E^1_{ox}, V	E^2_{ox}, V	E^1_{red}, V	E^2_{red}, V
1b	0.53	0.98	-1.11	-
2a	-	-	-0.93	-
2b	0.58	1.02	-0.89	-1.19
2c	0.91	1.11	-0.94	-1.09

III. EXPERIMENTAL SECTION

Purity of all compounds was checked by TLC method on Merck F_{254} silica plates. The spots were visualized when necessary in UV light and in iodine vapor. Chromatographic separations were carried out on silica gel (Merc, reinst) or Biotage SP1 HPLC using Biotage silica gel cartridges. Melting points were taken on a Stuart apparatus SMP 10, and ^{1}H NMR spectra were obtained on Bruker Avance 300 (300 MHz) spectrometer against TMS as an internal reference. UV spectra were recorded using Perkin-Elmer UV/VIS spectrometer Lambda 35. Water Alliance 2695 HPLC was used with XTerra® MS detector, mass spectra obtained in ESI+ mode, cone voltage 30V.

Melting points (T_m) and decomposition temperatures (T_{onset}) of chromophores were determined by Perkin Elmer STA 6000.

Cyclic voltammetry was recorded using Advanced Electrochemical System PARSAT 2273. Redox reactions of the compounds **1b**, **2a**, **2b**, **2c** were studied in 0,1M $TBAPF_6$/MeCN solution; glassy carbon disk (⦸ 6mm) served as a working electrode, Pt wire – as a counter electrode, and a saturated calomel electrode (SCE) fitted with a salt bridge – as a reference electrode. The dissolved oxygen was removed from solution by purging with argon.

4-Bromo-*N,N*-diphenylbenzenamine (4). To the solution of compound **3** (7.65 g, 31.2 mmol) in tetrachloromethane (80 mL) NBS (5.56 g, 31.2 mmol) was added, and the reaction mixture was refluxed for 4 h under argon atmosphere. The mixture was cooled to room temperature; the precipitate was filtered off and washed with tetrahloromethane. Solvent was removed under vacuum, and the resulting product was recrystallized from ethanol (120-130 mL) to give white powder, which contains compound **3** (~10%), compound **4** (~78%) and compound 4,4'-dibromotriphenylamine (~10%). This mixture was used as starting material for compounds **5** and **8**. The pure product was obtained by silica gel chromatography (tetrachloromethane/petroleum, 1:2 as eluent). Compound **3** R_f 0.51, compound **4** R_f 0.60, 4,4'-dibromotriphenylamine R_f 0.64. Compound **4** is white powder, m.p. 113-115 °C. 1H NMR spectrum in $CDCl_3$, δ, ppm (J, Hz): 7.24 (d, J = 8.8, 2H), 7.2-7.13 (m, 4H), 7.04-6.91 (m, 6H), 6.87 (d, J = 8.8, 2H). Mass spectrum (ESI+), m/z: calculated $C_{18}H_{15}BrN$ 325.2 $[M+H]^+$, found 323/325 $[M+H]^+$.

***N*^{1},*N*^{1}-Dibutyl-*N*^{4},*N*^{4}-diphenylbenzene-1,4-diamine (5).** The suspension of $Pd(OAc)_2$ (0.114 g, 0.25 mmol), BINAP (0.153 g, 0.25 mmol), compound **4** (4.0 g, 12.3 mmol) in toluene (12 mL) was stirred for 20 minutes at room temperature and KO*t*Bu, dibutilamine (2.5 mL, 14.8 mmol) was added, followed by 12 mL of toluene. The mixture was heated at 100 – 105 °C temperature under argon atmosphere, till complete consumption of starting materials was observed. The reaction was monitored by thin-layer chromatography (tetrachloromethane/petroleum, 1:5 as eluent). The mixture was cooled to room temperature, diluted with MTBE (40 mL), washed with water (20 mL). The water extract was extracted two times with MTBE (2×40 mL). The combined organic extracts were washed two times with water (2×20 mL) and dried over Na_2SO_4. After removal of the solvent, the resulting brown oil (4.2 g) was used as starting material for compound **6**. This oil contains compound **5** (~80%) and compound **3** (~10%). The pure product was obtained by column chromatography on silica gel (toluene/petroleum, 1:2 as eluent). Compound **5** R_f 0.46, compound **3** R_f 0.78. 1H NMR spectrum in $CDCl_3$, δ, ppm (J, Hz): 7.16-7.04 (m, 4H), 7.03-6.86 (m, 6H), 6.86-6.74 (m, 2H), 6.57-6.42 (m, 2H), 3.29-3.00 (broad signal, 4H), 1.55-1.43 (m, 4H), 1.34-1.17 (m, 4H,), 0.88 (t, J = 7.3, 6H). Mass spectrum (ESI+), m/z: calculated $C_{26}H_{33}N_2$ 373.6 $[M+H]^+$, found 373.2 $[M+H]^+$.

4-((4-Dibutylamino)phenyl)(phenyl)amino)benzaldehyde (6). DMF (0.48 mL, 6.1 mmol) was cooled in an ice bath to 0 °C, and $POCl_3$ (0.53 mL, 5.7 mmol) was added with stirring. The reagent was allowed to warm to room temperature and compound **5** (1.06 g, 2.8 mmol) dissolved in dichloromethane (1 mL) was added with stirring. The reaction mixture was heated for 3 h at 80 °C temperature under argon atmosphere. After cooling it was poured into crushed ice (50 g) and neutralized till pH 8 with 40% solution of NaOH keeping temperature below 20 °C by external cooling and adding crushed ice. The water solution was extracted two times with dichloromethane (2×70 mL). The combined organic extracts were washed two times with water (2×40 mL) and dried over Na_2SO_4. After removing the solvent, the resulting crude product was purified by column chromatography on silica gel (ethyl acetate/ hexane, 1:4 as eluent) and was taken fraction with R_f 0.45. Compound **6** is yellowish oil, yield is 0.68 g (60%). 1H NMR spectrum in $CDCl_3$, δ, ppm (J, Hz): 9.67 (s, 1H), 7.55 (d, *J* = 8.7, 2H), 7.28-7.19 (m, 2H), 7.15-7.09 (m, 2H), 7.07-6.99 (m, 1H), 6.93 (d, *J* = 8.9, 2H), 6.85 (d, *J* = 8.7, 2H), 6.52 (d, *J* = 8.9, 2H), 3.22-3.13 (m, 4H), 1.56-1.44 (m, 4H), 1.32-1.23 (m, 4H), 0.88 (t, *J* = 7.3, 6H). Mass spectrum (ESI+), m/z: calculated $C_{27}H_{33}N_2O$ 401.6 $[M+H]^+$, found 401.2 $[M+H]^+$.

4,4'-(4-Bromophenylazanediyl)dibenzaldehyde (8). DMF (36.8 mL, 0.48 mol) was cooled in an ice bath to 0 °C, and $POCl_3$ (48.0 mL, 0.52 mol) was added dropwise with stirring not allowing temperature to rise above 10 °C. Vilsmeier-Haack reagent was solid at room temperature, so it was warmed to 30 – 40 °C and compound **4** containing mixture was added in portion with stirring. The mixture was heated for 7 h at 95 – 100 °C under argon atmosphere After cooling it was poured into crushed ice and neutralized till pH 8 with 40% solution of NaOH keeping temperature below 20 °C by external cooling and adding crushed ice. At the end of the neutralization bulk precipitates formed. Water (500 mL) was added in order to dissolute inorganic salts, and precipitate was separated by filtration and thoroughly washed with water. Crude product, which also contains compounds **8** and 4-[(4-bromphenyl)(phenyl)amino]benzaldehyde in 3:1 ratio was dried on air and by column chromatography (silica gel, dichloromethane as eluent) was separated with compound **8** enriched fraction. This fraction, which contains compound **8** and 4,4'-(phenylazanediyl)dibenzaldehyde, was used as starting material for compound **9**. The pure product was obtained by 0.6 m long silica gel column (dichloromethane as eluent). The fraction content was determined by mass spectrometer (delay time for 4,4'-(phenylazanediyl)dibenzaldehyde is 7.8 min., compound **8** – 10.4 min.). Pure fraction yield is 2.0 g (24%). Compound **8** is yellowish crystalline substance, m.p. 183-5 °C. 1H NMR spectrum in $CDCl_3$, δ, ppm (J, Hz): δ 9.84 (s, 2H), 7.72 (d, *J* = 8.6, 4H), 7.43 (d, *J* = 8.7, 2H), 7.11 (d, *J* = 8.6, 4H), 6.99 (d, *J* = 8.7, 2H). Mass spectrum (ESI+), m/z: calculated $C_{20}H_{15}BrNO_2$ 381.3 $[M+H]^+$, found 380.0/382 $[M+H]^+$.

***N*^{1},*N*^{1}-Dibutyl-*N*^{4},*N*^{4}-bis(4-(4-methyl-1,3-dioxolan-2-yl)phenyl) benzene-1,4-diamine (9).** To the solution of compound **8** (1.90 g, 5.0 mmol) in benzene (30 mL) propan-1,2-diole (0.88 mL, 12.0 mmol) and two drops of konc. HCl were added. Water was continuously removed by azeotropic distillation employing a Dean-Stark trap. The reaction was monitored by thin-layer chromatography (dichloromethane as eluent). After 72 hours of boiling intermediate-monoprotected compound was formed. Propan-1,2-diole and two drops of konc. HCl were added, and boiling continued for 96 h. Acidic solution was neutralized with saturated solution of $NaHCO_3$, washed with water, dried over KOH for 24 h. After filtration and removal of the solvent under vacuum the resulting product – bright yellow oil was dried under dynamic vacuum. Yield is quantitative - 2.4 g. 1H NMR spectrum in $CDCl_3$, δ, ppm (J, Hz): 7.37-7.24 (m, 6H), 7.04-6.93 (m, 4H), 6.91-6.82 (m, 2H, Ar), 5.81 (s, 1H), 5.68 (s, 1H), 4.38-4.17 (m, 3H), 4.10-4.00 (m, 1H), 3.60-3.42 (m, 2H), 1.31 (dd, *J* = 15.9, 6.1, 6H). To the solution of protected compound (2.00 g, 4.0 mmol) in toluene $Pd(OAc)_2$ (0.037 g, 0.08 mmol), BINAP (0.050 g, 0.08 mmol) was added under argon, and stirring continued for 30 minutes. To this suspension KO*t*Bu, dibutilamine (2.5 mL, 14.8 mmol) was added, and the reaction mixture was heated at 90 °C temperature for 20 h under argon atmosphere. The work-up of the reaction mixture was the same as for compound **5**. Crude product was purified by column chromatography on silica gel (diizopropylether/ petroleum, 10:1, as eluent). Amine **9** R_f 0.59. Yield is 1.3 g (60%), amine **9** is yellowish oil. Mass spectrum (ESI+), m/z: calculated $C_{34}H_{45}N_2O_4$ 544,74 $[M+H]^+$, found 545.4 $[M+H]^+$.

4,4'-(4-(Dibutylamino)phenylazanediyl)dibenzaldehyde (10). The mixture containing compound **9** was dissolved in minimal volume of MTBE (8 mL), and 50 μL of konc. HCl was added under argon atmosphere. The solution was grown muddy and oily precipitate formed, which contained only sign of impurity **8**. The salt was washed two times with MTBE (2×5 mL), dissolved in dichloromethane (20 mL), and solution was hydrolyzed, washed two times with saturated $NaHCO_3$ (2×10 mL), dried over Na_2SO_4. After removing the solvent, the resulting oil was purified by column chromatography on silica gel (diizopropylether/ petroleum, 10:1, as eluent) compound **10** R_f 0.53, impurity **8** R_f 0.38). 1H NMR spectrum in $CDCl_3$, δ, ppm (J, Hz): 9.80 (s, 2H), 7.68 (d, *J* = 8.3, 4H), 7.12 (d, *J* = 8.3, 4H), 6.98-6.85 (m, 2H), 6.63-6.47 (m, 2H), 3.28-3.11 (broad signal, 4H), 1.61-1.44 (broad signal, 4H), 1.35-1.20 (m, 4H), 0.90 (t, *J* = 7.3, 6H). Mass spectrum (ESI+), m/z: calculated $C_{28}H_{33}N_2O_2$ 429.6 $[M+H]^+$, found 429.2 $[M+H]^+$

2-(4-((4-Dibutylamino)phenyl)(phenyl)amino) benzilidene-1*H*-indene-1,3(2*H*)-dione (1b). Compound **6** was dissolved in minimal volume of ethanol with heating, and indan-1,3-dione, piperidine acetate was added with stirring. The reaction mixture was boiled for 20 minutes, and then it was refrigerated. Solids were filtered and washed with ethanol. Crude product yield is 0.52 g (65%). To separate the starting material from the reaction mixture, it was stirred with MTBE. The resulting mixture was dissolved in minimal volume of dichloromethane and adsorbed on silica gel (1.2 g). Silica gel with adsorbed on it resulting mixture was brought

up on column and purified with chromatography (ethyl acetate petroleum/ petroleum, 1:3 as eluent). Compound **1b** R_f 0.64, starting material **6** R_f 0.74, indan-1,3-dione self-condensation product R_f 0.55. Compound **2a** is violet crystalline substance (0.35 g, 44%); mp.145-6 °C. 1H NMR spectrum in DMSO-d_6, δ, ppm (J, Hz): 8.40 (d, *J* = 9.1, 2H), 7.88-7.77 (m, 4H), 7.60 (s, 1H), 7.44-7.32 (m, 2H), 7.28-7.16 (m, 3H), 7.02 (d, *J* = 9.0, 2H), 6.68 (d, *J* = 9.1, 2H), 6.62 (d, *J* = 9.0, 2H), 3.38-3.16 (overlap with water signal, m, 4H), 1.52-1.36 (m, 4H), 1.34-1.19 (m, 4H), 0.86 (t, *J* = 7.3, 6H). Mass spectrum (ESI+), m/z: calculated $C_{36}H_{37}N_2O_2$ 529.7 $[M+H]^+$, found 529.3 $[M+H]^+$.

2,2'-(4,4'-(4-(Dibutylamino)phenylazanediyl)bis(4,1-phenylene)bis(methanylidene))bis(1*H*-indene-1,3(*2H*)-dione (2b). Amine **9** (0.194 g, 0.36 mmol) was dissolved in minimal volume of *n*-butanol (3 mL) with heating at 40 °C under argon atmosphere. 100 μL konc. HCl and indan-1,3-dione (0.135 g, 0.92 mmol) were added, and the reaction mixture was refluxed for 1 ½ h. Then the mixture was cooled to room temperature and solids were filtered and washed with ethanol. Salt **11** was dissolved in chloroform, and solution was hydrolyzed, washing in separating funnel with saturated $NaHCO_3$ (2×15 mL). Solution was dried over Na_2SO_4, and solvent was removed under vacuum. Compound **2b** is dark violet crystalline substance. Compound **4** yield is 0.19 g (81%); mp. 81-2 °C; R_f 0.29 (dichloromethane as eluent). 1H NMR spectrum DMSO-d_6, δ, ppm (J, Hz): 8.57 (d, *J* = 8.9, 4H), 8.05-7.90 (m, 8H), 7.78 (s, 2H), 7.19 (d, *J* = 8.9, 4H), 7.08 (d, *J* = 9.0, 2H), 6.75 (d, *J* = 9.0, 2H), 3.50-3.30 (overlap with water signal, 4H), 1.64-1.45 (m, 4H), 1.42-1.28 (m, 4H), 0.95 (t, *J* = 7.3, 6H). Mass spectrum (ESI+), m/z: calculated $C_{46}H_{41}N_2O_4$ 685.8 $[M+H]^+$, found 685.4 $[M+H]^+$.

4-Nitro-*N,N*-diphenylaniline (**13**). To a cooled in ice bath suspension of NaH (60% dispersion in oil, 1.82 g, 0.042 mol) in 10 mL of DMF diphenylamine (**12**) (3.38 g, 0.02 mol) in 5 mL of DMF was added dropwise under Ar. The mixture was allowed to warm to the room temperature and stirring continued for 1 h. Then 1-fluoro-4-nitrobenzene (3.0 g, 0.021 mol) was added, and the mixture was stirred for 24 h. The reaction mixture was poured onto ice, the precipitate filtered off, washed with water and dried. Compound **13** was recrystallized from MTBE. Yield 4.56 g, (79%), yellow crystals, m.p. 142 - 144 ºC. 1H NMR spectrum in $CDCl_3$, δ, ppm (J, Hz): 8.02 (d, J = 9.3, 2H), 7.38-7.34 (m, 4H), 7.23-7.11 (m, 6H), 6.90 (d, J=9.3, 2H).

***N*^{1},*N*^{1}-Diphenylbenzene-1,4-diamine** (**14**). To a solution of compound **13** (2.9 g, 0.01 mol) in 90 mL of acetic acid Sn (3 g) was added, and the mixture was heated to reflux for 10 h. Water (120 mL) and dichloromethane (200 mL) were added, and the mixture was shaken with 40% NaOH solution till the aqueous layer became alcaline. Dichloromethane layer was separated, washed with water and dried over magnesium sulfate. The solvent was partially removed (till the volume of the solution 30 mL), and 50 mL of hexane was added. Precipitate was filtrated and dried, yield 2.59 g (86%) white crystals, m.p. 199 – 200 ºC. 1H NMR spectrum in DMSO-d_6, δ, ppm (J, Hz): 9.87 (s, 1H), 7.46 (d, J = 7.8, 2H), 7.23-7.18 (m, 4H), 6.97-6.83 (m, 8H), 1.96 (s, 3H). This product was *N*-(4-diphenylamino-phenyl)acetamide. Dioxane (16 mL), water (50 mL) and conc. HCl (10 mL) were added and the mixture refluxed with stirring for 2 days, made alkaline with $NaHCO_3$ and extracted with ethyl acetate. Organic layer was separated, washed with water and dried over sodium sulphate. Evaporation afforded pale brown crystals of compound **14**, yield 1.92 (87%), m.p. 154-6 ºC. 1H NMR spectrum in $CDCl_3$, δ, ppm (J, Hz):7.16-7.22 (m, 4H), 6.89-7.04 (m, 8H), 6.65 (d, J=9, 2H), 3.55 (s, 2H).

2-(4-Bromophenyl)-4-methyl-1,3-dioxolane (15). 4-Bromobenzaldehyde (5.0 g, 0.027 mol), propane-1,2-diole (2.2 mL, 0.029 mol) and *p*-TsOH (0.5 g) in 75 mL benzene were refluxed for 3 days. Water was continuously removed employing a Dean-Stark trap. Mixture was cooled, washed with $NaHCO_3$ and dried over NaOH. After filtration and removal of the solvent under vacuum the resulting product – bright yellow oil was dried under dynamic vacuum. Yield is quantitative – 6.5 g.

4,4'-(4-Diphenylamino)phenylazanediyl)dibenzaldehyde (16). To a Schlenk tube under Ar compound **14** (2.1 g, 8.6 mmol), $Pd^0(dba)_2$ (140 mg), toluene (11 mL) and tri-*tert*-butylphosphine (45 μL) were added, and the mixture was stirred for ¼ h, then compound **15** (1 g, 3.8 mmol) and NaO*t*Bu (0.86 g, 8.9 mmol) were added, and the tube was sealed and heated with stirring at 90 ºC for 3 days. The reaction mixture was then poured into water and extracted with MTBE. Organic extracts were washed with water and dried over Na_2SO_4. After removal of the solvent, the crude product was purified by column chromatography on silica gel. By-products were separated with CH_2Cl_2 : hexane 5:1, then with CH_2Cl_2 pure compound **16** was eluted. Yield 0.8 g (45%) of yellow crystals, m.p. 84 – 85 ºC. 1H NMR spectrum in $CDCl_3$, δ, ppm (J, Hz): 9.81 (s, 2H), 7,79 (d, J = 8.5, 4H), 7.34-7.22 (m, 4H), 7.13 (d, J=8.5, 4H), 7.06-6.93 (m, 10H).

2,2'-(4,4'-(4-(Diphenylamino)phenylazanediyl)bis(4,1-phenylene)bis (methanylidene)bis(1H-indene-1,3(2H)-dione) (2c). Compound **16** (0.47 g, 1 mmol) and compound **7** (0.3 g, 2 mmol) in 10 mL of n-butanol were refluxed for 2 h with stirring. After cooling the precipitate was filtered off, washed with ethanol and dried. Compound **2c** was recrystallized from ethylacetate-hexane. Yield 0.68 g (94%) of brownish red crystals, m.p. 250-5 ºC. **MS ESI+** *m/z* calculated $C_{50}H_{32}N_2O_4$ 724.6 $[M+H]^+$, found 725.4 $[M+H]^+$. 1H NMR spectrum in $CDCl_3$, δ, ppm (J, Hz): 8.53 (d, J = 8.9, 4H), 7.95-7.86 (m, 8H), 7.74 (s, 2H), 7,32-7.28 (m, 4H), 7.18 (d, J = 8.9, 4H), 7.15-6.97 (m, 10H).

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Jekaterina Sirotkina, Lauma Laipniece, Kristīne Lazdoviča, Baiba Turovska, Valdis Kampars. Aizvietotu p-fenilenediamīna donoru un 1*H*-indan-1,3(2*H*)-diona akceptoru saturošu hromoforu sintēze un īpašības.
Lai novērtētu stipru elektrondonoru grupu ievadīšanas trifenilamīna *p*-pozīcijā ietekmi uz iegūto savienojumu fizikālām īpašībām, sintezēti jauni hromofori *Knoevenagel* kondensācijas reakcijā starp 4-((4-dibutilamino)fenil)(fenil)amino)benzaldehīdu, 4,4'-(4-(dibutilamino)fenilazanediil)dibenzaldehīdu un 4,4'-(4-difenilamino)fenilazanediil)dibenzaldehīdu un 1*H*-indan-1,3(2*H*)-dionu. Hromoforu iegūšanas optimizēšanai pētīta 4-brom-*N,N*-difenilbenzenamīna un N^1,N^1-dibutil-N^4,N^4-difenilbenzen-1,4-diamīna *Vilsmeier-Haack* formilēšanas reakcija. Konstatēts, ka tieša N^1,N^1-dibutil-N^4,N^4-difenilbenzen-1,4-diamīna formilēšana neļauj ar apmierinošu iznākumu iegūt 4,4'-(4-(dibutilamino)fenilazanediil)dibenzaldehīdu, bet to ir iespējams iegūt divu stadiju procesā: vispirms aizsargājot 4,4'-(4-bromfenilazanediil)dibenzaldehīda karbonilgrupas un tad ievadot dibutilaminogrupu Pd katalizētā reakcijā ar sekojošu aizsarggrupu noņemšanu. 4,4'-(4-Difenilamino)fenilazanediil)dibenzaldehīds iegūts pallādija(0) katalizētā N^1,N^1-difenilbenzen-1,4-diamīna divkāršā *N*-arilēšanas reakcijā ar 2-(4-bromfenil)-4-metil-1,3-dioksolānu. Iegūtajiem hromoforiem piemīt laba šķīdība organiskajos šķīdinātājos. Ievadot difenilaminogrupu trifenilamīnā, iegūto savienojumu termiskās īpašības praktiski nemainījās, turpretī dibutilaminogrupas ietekme ir ievērojama. *UV-Vis* spektrā novērota negatīva solvatohromija un neliela lādiņa pārneses joslas batohroma nobīde. Hromoforu, kas satur molekulā divus trešējo amīnu fragmentus, anodoksidācija ir neapgriezeniska un darbā pētīta aizvietotāju ietekme uz oksidācijas spēju. Parādīts, ka *N*-4 slāpekļa atoms ir primārais reakcijas centrs anodoksidācijā. Hromoforu reducēšanās notiek pie -1 V un 1*H*-indan-1,3(2*H*)-diona fragmenta reducēšanas potenciāls nav jūtīgs pret aizvietotāju dabu hromofora molekulā.

Екатерина Сироткина, Лаума Лайпнеце, Кристина Лаздовича, Байба Туровска, Валдис Кампар. Синтез и свойства хромофоров содержащих замещеного п-фенилендиамина донорную группу и 1Н-индан-1,3(2Н)-диона акцепторную группу.
С целью изучить влияние введения сильных электрондонорных групп в п-позицию TPA, в реакции Knoevenagel конденсации 4-((4-дибутиламино)фенил)(фенил)амино)бензальдегида, 4,4'-(4-(дибутиламино) фенилазанедиил)дибензальдегида и 4,4'-(4-дифениламино) фенилазанедиил)дибензальдегида с 1Н-индан-1,3(2Н)-дионом были получены новые хромофоры. Для оптимизации получения хромофоров было изучено Vilsmeier-Haack формилирование 4-бром-N,N-дифенилбензенамина и N1,N1-дибутил-N4,N4-дифенилбензен-1,4-диамина. Мы констатировали, что напрямую формилирует N1,N1-дибутил-N4,N4-дифенилбензен-1,4-диамин, выход 4,4'-(4-(дибутиламино)фенилазанедиил)дибензальдегида ничтожен, поэтому для его получения был использован 4,4'-(4-бромфенилазанедиил)дибензальдегид. 4,4'-(4-Дифениламино)фенилазанедиил)дибензальдегид был получен в реакции N-арилирования 2-(4-бромфенил)-4-метил-1,3-диоксолана в условиях катализации палладием. Полученные хромофоры хорошо

растворимы в органических растворителях. Введение в TPA дифениламиногруппы практически не влияет на термические свойства по сравнению с введением в TPA дибутиламиногруппы. В UV-Vis спектре видна отрицательная сольватохромия и небольшой батохромный сдвиг полосы переноса заряда. Хромофоры содержащие в структуре третичный амин участвуют в обратимой оксидации у анода, также изучается влияние заместителей на окисидацию хромофоров. Атом азота N-4 является первичным центром рекции оксидации у анода. Реакция восстановления хромофоров у катода происходит при -1 V. Восстановительный потенциал 1H-индан-1,3(2H)-диона групы практически не зависит от эффекта заместителей.