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Synthesis, photophysical and nonlinear optical properties of [1,2,5]oxadiazolo[3,4-*b*]pyrazine-based linear push-pull systems

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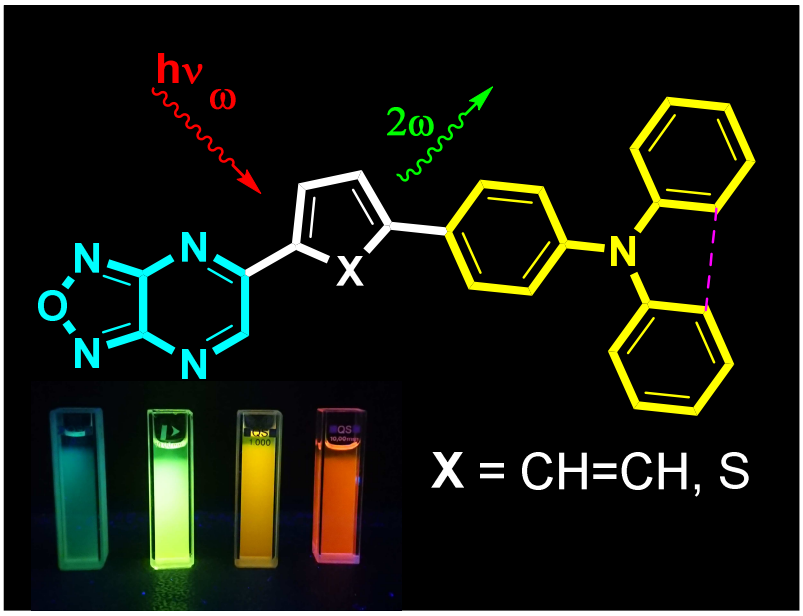
Graphical Abstract



Abstract

A series of D-π-A chromophores based on [1,2,5]oxadiazolo[3,4-*b*]pyrazine electron-withdrawing group has been designed. The influence of the π-conjugated linker (1,4-phenylene and 2,5-thienylene) and the amino-electron-donating group (diphenylamino and carbazol-9-yl) was studied by cyclic voltammetry, UV-Vis and emission spectroscopy. The second order nonlinear optical properties were also studied using the electric field induced second harmonic generation (EFISH) method. The experimental results have been rationalized by theoretical DFT calculations.

Keywords: nitrogen heterocycles; donor–acceptor systems; nonlinear optic; fluorescence; intramolecular charge transfer

1. Introduction

Organic nonlinear optical (NLO) materials have attracted considerable attention in recent years because of their potential applications in various fields of optoelectronics and photonics, including optical communications, optoelectronic transfer, optical signal process and optical data storage [1]. The main advantages of these materials are high NLO coefficients, ultrafast optical responses, flexible molecular design and synthesis and higher optical damage threshold, as compared to traditional inorganic solids. Generally, the NLO properties of organic materials are dependent on the molecular structures of chromophores. Typically, in order to show a significant second-order NLO response, a molecule must be non-centrosymmetric, with intramolecular charge transfer (ICT) transitions at relatively low energy and characterized by a large transition dipole moment and a large difference between the excited state and the ground state molecular dipole moment [1e]. This can be achieved in linear organic molecules by connecting an electron-

donor and an electron-acceptor group through a π-conjugated polarizable spacer, as it occurs in classical organic dipolar push–pull systems [2].

Pyrazine is a nitrogen based heterocyclic compound with a rigid planar conjugated structure. Due to the electron-deficient character of the pyrazine, the pyrazinyl fragment can be used as electron-withdrawing group in push-pull structures. The incorporation of pyrazine units in luminescent materials has been recently reviewed [3]. Moreover, it has been shown that push-pull pyrazine derivatives exhibit interesting second-order (frequency doubling) [4] and third-order (two photon absorption) [5] NLO properties.

It has been demonstrated that [1,2,5]oxadiazolo[3,4-*b*]pyrazine (furazanopyrazine) exhibits higher electron-withdrawing character than similar non-annulated pyrazine analogues [6]. Recently, the [1,2,5]oxadiazolo[3,4-*b*]pyrazine core has been used as an acceptor part of push-pull molecules exhibiting pronounced fluorescence in the solid state and sensitivity towards nitroaromatic compounds [7].

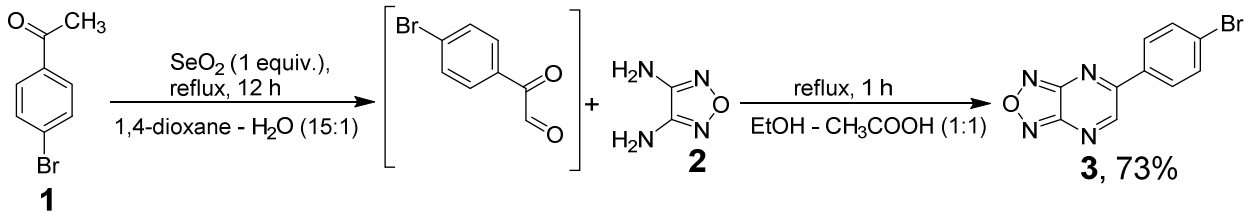
This work represents further extension of our previous research focusing on the design of novel fluorophores that incorporate diazine scaffold. In this contribution we describe the synthesis of a new series of D–π–A [where A equals to the 1,2,5-oxadiazolo[3,4-*b*]pyrazine acceptor, D represents triphenylamine or carbazole donors, and π involves thienylene or phenylene groups] push-pull chromophores **7a,b** and **8a,b** and systematic investigation of their photophysical and second order NLO properties. The influences of the type of the π- linker as well as the nature of the electron-donating group on the photophysical properties were thoroughly studied and structure-property relationships were elucidated.

2. Results and Discussion

Synthesis

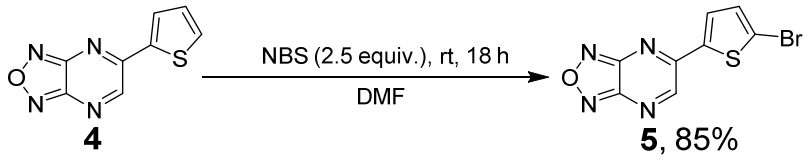
The synthesis of the linear push-pull systems required 5-(4-bromophenyl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (**3**) and 5-(5-bromothiophen-2-yl)-[1,2,5]oxadiazolo[3,4-

b]pyrazine (**5**) as starting materials. Compound **3** was prepared via a two-step procedure from commercially available 4'-bromoacetophenone (**1**) in 73% overall yield (Scheme 1).



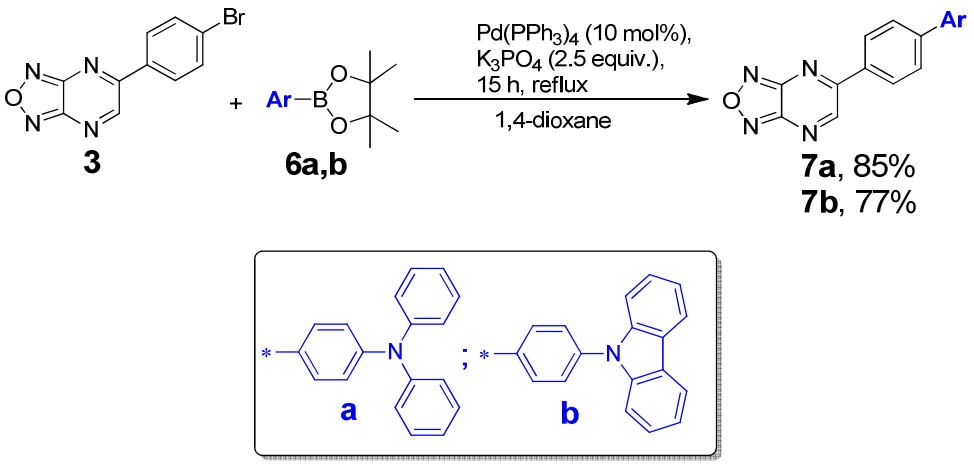
Scheme 1. Synthesis of 5-(4-bromophenyl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (**3**).

The second starting material (**5**) was obtained by bromination of previously described 5-(1-benzothiophen-3-yl)pyrimidine (**4**) [7] with an excess of *N*-bromosuccinimide in 85% yield.

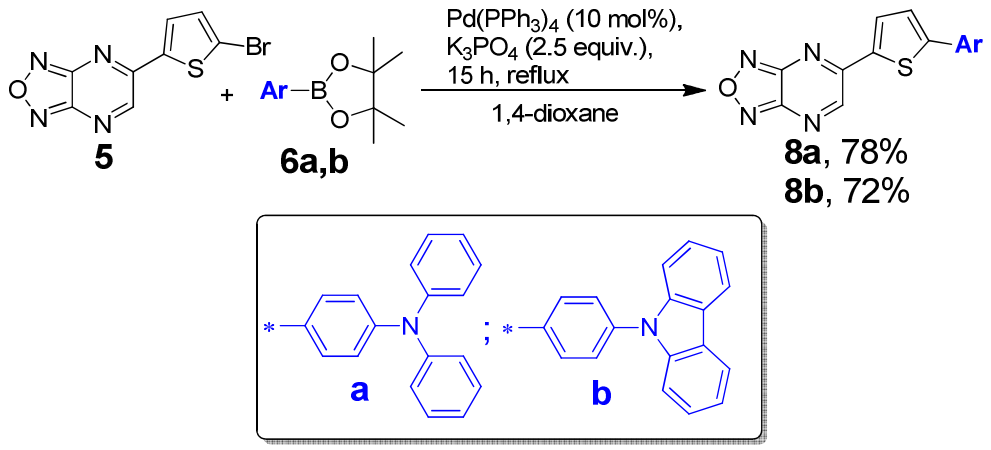


Scheme 2. Synthesis of 5-(5-bromothiophen-2-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (**5**).

The target chromophores **7a-b** and **8a-b** were synthesized in high yields through the Suzuki-Miyaura cross-coupling reactions shown in Schemes 3 and 4. Furazanopyrazines **3** and **5** were coupled with the corresponding pinacol esters of 4-(diphenylamino)phenylboronic (**6a**) and 9*H*-carbazole-9-(4-phenyl)boronic (**6b**) acids under reflux in 1,4-dioxane by using $Pd(PPh_3)_4$ as catalyst. These reactions afforded the corresponding D-π-A dyes **7a-d** and **8a-d** in good yields (Schemes 3 and 4).



Scheme 3. Synthesis of 5-[4-(heteroaryl)phenyl]-[1,2,5]oxadiazolo[3,4-*b*]pyrazines (**7a,b**).



Scheme 4. Synthesis of 5-[5-(heteroaryl)thiophen-2-yl]-[1,2,5]oxadiazolo[3,4-*b*]pyrazines (**8a,b**).

Electrochemical properties

Electrochemical behavior of compounds **7** and **8** was studied by cyclic voltammetry (CV) in CH_2Cl_2 containing Bu_4NPF_6 electrolyte at a scan rate of 0.1 V/s. The working electrode was a glassy carbon disk, Pt wire was used as the counter electrode and an Ag wire as a reference electrode. Ferrocene was used as an internal reference for potential measurements. The first oxidation/reduction peak potentials and their differences are listed in Table 1 and CV diagrams are shown in Figure 1.

Table 1: Electrochemical data of compounds

Comp.	$E_{1/2}^{ox1}$ [V][a]	$E_{1/2}^{red1}$ [V][a]	ΔE [V][b]	E_{HOMO} [eV][c]	E_{LUMO} [eV][c]	λ_{max} [nm][d]
7a	0.55	–1.11	1.66	–5.33	–3.67	746
7b	0.95[e]	–1.10	2.05	–5.73	–3.69	604
8a	0.57	–1.14	1.71	–5.35	–3.64	727
8b	0.96[e]	–1.09	2.05	–5.74	–3.69	606

[a] All potentials are given versus ferrocene. [b] $\Delta E = E_{1/2}^{ox1} - E_{1/2}^{red1}$. [c] $E_{HOMO/LUMO} = -(E^{ox1/red1}+4.8)$. [d] Calculated λ_{max} values (λ=1241/ΔE). [e] Irreversible peaks *E*p

Compounds **7b** and **8b** bearing the carbazole moiety as an electron-donating group exhibit a first irreversible oxidation process at 0.95 and 0.96 V *vs.* ferrocene. When the donor is the diphenylamino moiety, the first oxidation is reversible and measured $E_{1/2}$ are much lower (0.55 V for **7a** and 0.57 V for **8a**; see Figure 1) in accordance with the stronger electron-donating effect of the diphenylamino group. For these two compounds, a second irreversible oxidation peak can be observed at the higher potential that modifies the reversibility of the first system, on the reverse scan.

All compounds bear the same oxadiazolopyrazine electron-withdrawing group. For this reason, the same behavior can be observed on reduction when scanning from 0 to –2 V. All compounds show a first reversible reduction around –1.1 V *vs.* Fc and a second quasi-reversible system around –2 V (scan rate = 0.1 V/s). The latter becomes reversible when the scanning rate is increased to 1 V/s (Figure S25). The obtained half-wave potentials for both systems are similar regardless of the nature of the electron-donating moieties and of the π-conjugated linker. This trend indicates a weak interaction between the donor and the acceptor.

The HOMO/LUMO energies were calculated from potential values (the first oxidation and reduction processes) to evaluate the electrochemical band gap. The E_{LUMO} remains unaltered as all chromophores showed the same reduction behavior. On the other hand, the E_{HOMO} of diphenylamino derivatives is higher leading to a decreased band gap for compounds **7a** and **8a**. These results correspond to the evolution of λ_{max} values obtained from the electronic spectra.

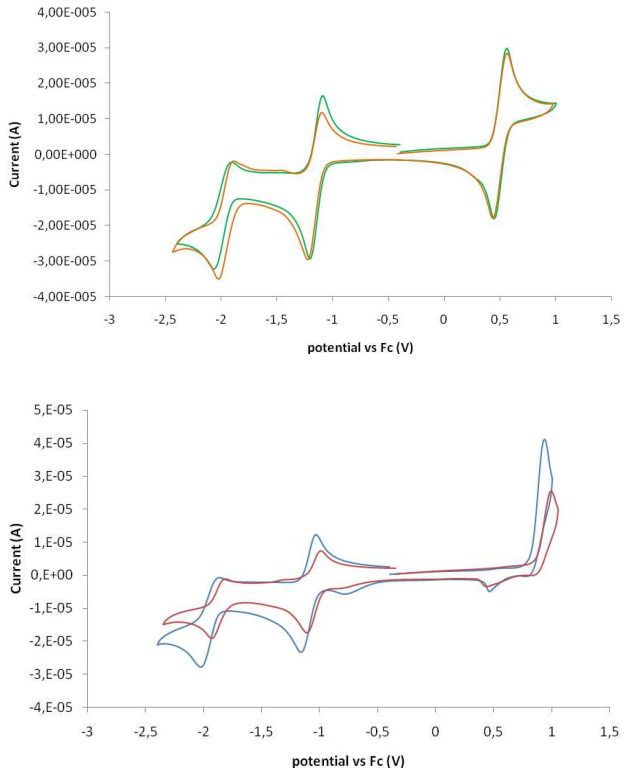


Figure 1. Cyclic voltammograms of **7a** (*green*), **8a** (*orange*) **7b** (*blue*) and **8b** (*red*) in CH_2Cl_2 solutions.

Photophysical properties

The photophysical properties of compounds **7** and **8** have been studied in various aprotic solvents of increasing polarity and the results are summarized in Table 2. All compounds are emissive in *n*-heptane. Carbazole derivatives **7b** and **8b** are also emissive in 1,4-dioxane but no emission is observed in solvents of higher polarity. For push-pull derivatives, such observation is rationalized by decreased emission intensity observed in polar solvents due to lowered energies of the ICT excited state [8]. Figure 2 shows the normalized absorption and emission spectra in *n*-heptane. As expected, the replacement of the 1,4-phenylene linker (compounds **7**) by a 2,5-thienylene one (compounds **8**) induces a red shift of both absorption and emission bands as well as increases the molar extinction coefficient due to a better charge transfer through the heterocycle [9]. Similarly, to previous observation [10], the diphenylamino derivatives exhibited red-shifted absorption and emission. This effect is more pronounced than changing the

π-conjugated linker. The absorption and emission maxima increase in the following order **7b** < **8b** < **7a** < **8a**. Compound **8b** exhibited the highest emission quantum yield in *n*-heptane (Φ_F = 0.96). The lowest value was observed for compound **7b** (Φ_F = 0.06), but this compound exhibited much higher quantum yield in 1,4-dioxane (Φ_F = 0.29). Figure 3 shows the color of *n*-heptane solutions of compounds **7**-**8** under UV-irradiation.

Table 2: UV/Vis and PL data in various solvents for compounds **7** and **8**.

Compds	**Solvent**	λ_{abs} (ε) [nm] [(mM^{-1} cm^{-1}])]	λ_{em} [nm]	Φ_F[a]	**Stokes shift** [cm^{-1}]
7a	*n*-heptane	473 (18.4)	570	0.54	3598
	1,4-dioxane	466 (12.4)	-[b]	-[b]	-[b]
	CH_2Cl_2	485 (11.8)	-[b]	-[b]	-[b]
	MeCN	457 (16.4)	-[b]	-[b]	-[b]
7b	*n*-heptane	414 (12.3)	521	0.06	4961
	1,4-dioxane	401 (8.7)	619	0.29	8783
	CH_2Cl_2	403 (8.9)	-[b]	-[b]	-[b]
	MeCN	389 (15.1)	-[b]	-[b]	-[b]
8a	*n*-heptane	514 (33.2)	607	0.39	2980
	1,4-dioxane	511 (22.7)	-[b]	-[b]	-[b]
	CH_2Cl_2	544 (22.7)	-[b]	-[b]	-[b]
	MeCN	518 (20.7)	-[b]	-[b]	-[b]
8b	*n*-heptane	452 (25.4)	548	0.96	3875
	1,4-dioxane	450 (22.5)	627	0.35	6273
	CH_2Cl_2	463 (20.3)	-[b]	-[b]	-[b]
	MeCN	447 (22.6)	-[b]	-[b]	-[b]

[a]Fluorescence quantum yield (±10%) determined relative to 9,10-*bis*(phenylethynyl)antracene in cyclohexane (Φ_F = 1.00) [b]No emission detected

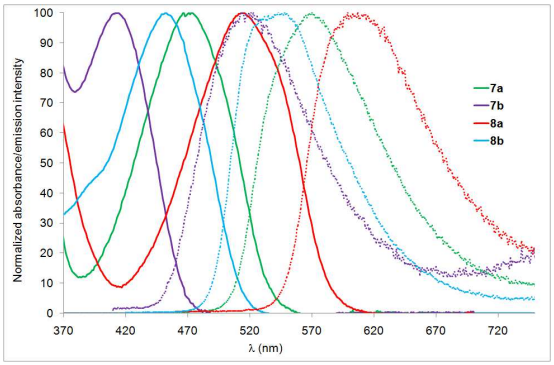


Figure 2: Normalized UV/Vis (*solid lines*) and emission spectra (*dashed lines*) of compounds **7** and **8** in *n*-heptane.

Figure 3: *n*-heptane solution under UV lamp irradiation (from left to right: **7b**, **8b**, **7a**, **8a**) c = 1-3×10^{-5} M. Photographs were taken in the dark upon irradiation with a hand-held lamp (λ_{em} = 366 nm)

Whereas only moderate absorption solvatochromism was observed for **7** and **8**, which does not seem to be correlated to the solvent polarity (the most red-shifted absorption bands are observed in CH_2Cl_2), a strong positive emission solvatochromism was observed for carbazole derivatives **7b** and **8b** as illustrated in Figures 4 and 5. It should be noted that emission solvatochromism was not observed for diphenylamino derivatives since the emission is fully quenched in solvents of higher polarity than *n*-heptane. This phenomenon, which is due to stabilization of the highly-polar emitting state by polar solvent, has been extensively described for push-pull derivatives [11]. It should be noted however that the quantum yield of compound **7b** is higher in 1,4-dioxane than in *n*-heptane, probably due to aggregation in this latter solvent.

The slope of the regression line of the emission maxima plotted versus the Dimroth-Reichardt polarity parameter ($E_T(30)$) is a way to evaluate the ICT [12]. The slope observed for compounds **7b** and **8b** (see Figure S1 in ESI) are similar or higher as compared to pyrazine push-pull derivatives with diphenylamino substituents and more extended π-conjugated linker [13], indicating that the oxadiazolo part significantly enhances the electron-withdrawing character of the pyrazine.

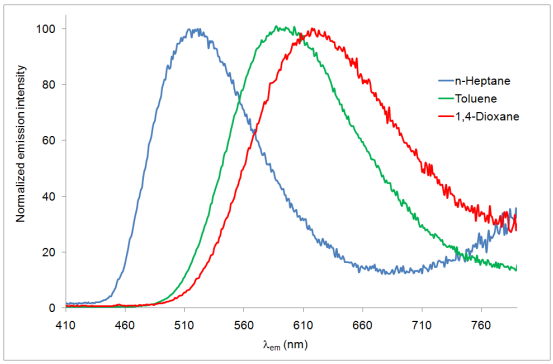


Figure 4: Normalized emission spectra of **7b** in different aprotic solvents

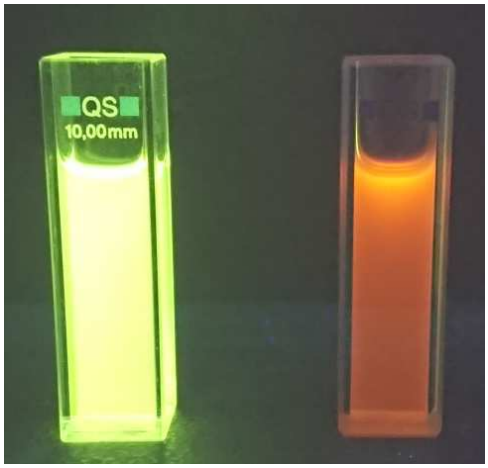


Figure 5: *n*-Heptane (left) and 1,4-dioxane (right) solution of **8b** under UV lamp $c = 3 \times 10^{-5}$ M. Photographs were taken in the dark upon irradiation with a hand-held lamp ($\lambda_{em} = 366$ nm)

Second order nonlinear optical properties

The second order NLO properties have been studied in chloroform solution by the electric-field induced second harmonic generation (EFISH) method at a non-resonant incident wavelength of 1907 nm. The second harmonic at λ = 953 nm is therefore well clear of the absorption bands of the chromophores. This method provides the NLO response as the scalar product between the permanent dipolar moment of the molecule $\vec{\mu}$ in fundamental state and the vector component of β described as $\beta_{//}$ [14]. The two level corrected $\mu\beta$ values ($\mu\beta_0$) have been also calculated [15]. The results are presented in Table 3. It should be noted that positive $\mu\beta$ values are obtained indicating that both ground and excited states are polarized in the same direction and that the excited state is more polarized than ground state, in accordance with the emission solvatochromism observation (for **7b** and **8b**). Compounds **8** exhibit higher NLO response than analogues **7** and the diphenylamino derivatives **a** show better $\mu\beta$ values than carbazole analogues **b**. These results are coherent with the electrochemical and photophysical observations indicating better ICT for compounds possessing 2,5-thienylene linker and diphenylamino electron-donating group. The figure of merit of compound **8a** appears particularly interesting.

Table 3: Results for EFISH measurements for compounds **7** and **8**.

	7a	**7b**	**8a**	**8b**
$\mu\beta$ (10^{-48} esu)[a]	700	70	1440	330
$\mu\beta_0$ (10^{-48} esu)[b]	485	53	892	237
$\mu\beta$/MW[c]	1.91	0.19	3.88	0.89

[a] $\mu\beta(2\omega)$ at 1907 nm in $CHCl_3$. Molecular concentrations used for the measurements were in the range of 10^{-3} to 10^{-2} M, $\mu\beta \pm 10\%$ [b]Two level corrected $\mu\beta$ values ($\mu\beta_0$) [14]. [c]Figure of merit (molecular nonlinearity) 10^{-48} esu g mol^{-1} [16]

DFT calculations

Spatial and electronic properties of compounds **7a**-**b** and **8a**-**b** were investigated using Gaussian®16W software [17] package at the DFT level. Optimized geometries, energies of the

frontier molecular orbitals, and ground state dipole moments μ and were calculated at DFT B3LYP/6-311+G(2df,p) level in $CHCl_3$ as shown in Table 4. The electronic absorption spectra and the first-order hyperpolarizabilities β were calculated by TD-DFT method using CAM-B3LYP/6-311+G(2df,p) in $CHCl_3$.

Table 4: DFT-calculated electronic parameters of **7** and **8**.

	7a	**7b**	**8a**	**8b**
E_{HOMO} (eV)[a]	–5.45	–5.83	–5.48	–5.83
E_{LUMO} (eV)[a]	–3.53	–3.61	–3.46	–3.58
ΔE (eV)[a]	1.92	2.22	2.02	2.25
μ (D)[a]	10.7	6.5	13.1	8.8
λ_{max}^{DFT} (nm/eV)[b]	422(2.94)	367(3.38)	479(2.59)	439(2.82)
$\beta(-2\omega,\omega,\omega)$ (10^{-30} esu)[b,c]	215	85	373	149

[a] Calculated at DFT B3LYP/6-311++G(2df,p) level in $CHCl_3$. [b] Calculated at TD-DFT (nstates = 8) CAM-B3LYP/6-311+G(2df,p) level in $CHCl_3$. [c] At 1907 nm in $CHCl_3$.

The calculated energies of the HOMO and the LUMO range from –5.83 to –5.45 and –3.61 and –3.46 eV (Figure 6), respectively. Both calculated and electrochemical HOMO-LUMO gaps obey the same trends and correlates tightly (Figure S2) and, therefore we can consider the used DFT method as reliable. In general, the lowest HOMO–LUMO gap has been calculated for chromophores in series **a** bearing *N*,*N*-diphenylamino donor. The carbazole-terminated chromophores **b** showed deepened HOMO. The gaps are slightly lower for chromophores **7** with 1,4-phenylene π-linker.

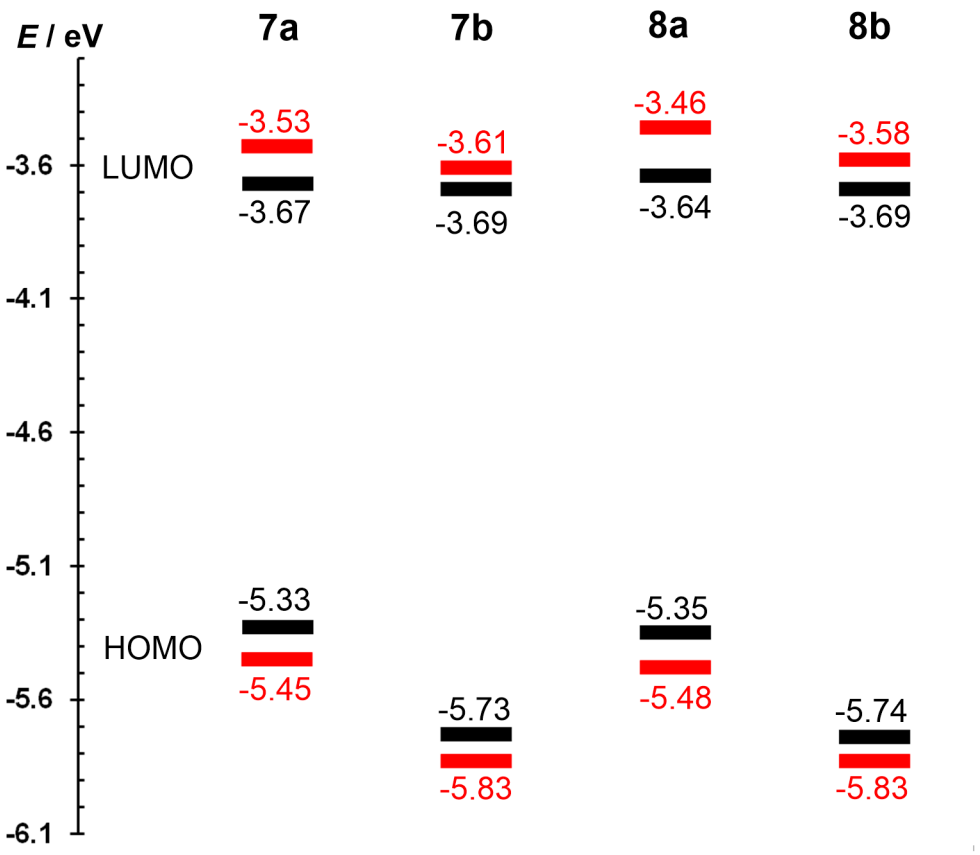


Figure 6: Energy level diagram showing the electrochemical (black) and calculated (red) HOMO/LUMO energies.

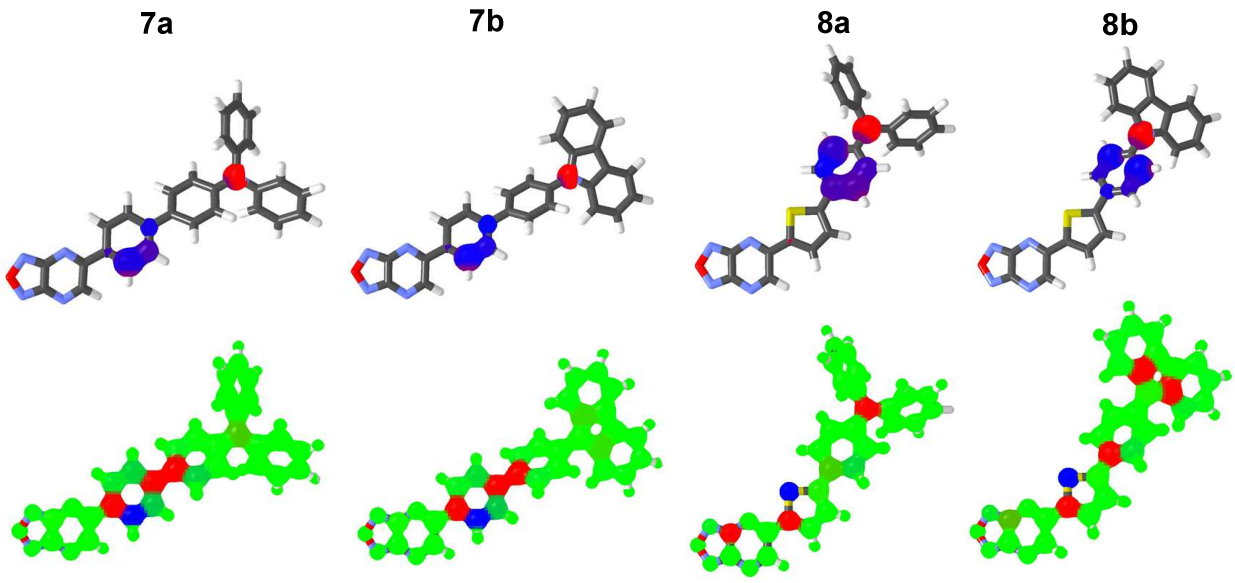


Figure 7: HOMO (*red*) and LUMO (*blue*) localizations (*above*) and Mulliken charges (*below*) in chromophores **7a**-**b** and **8a**-**b**.

Figure 7 shows optimized geometries, HOMO/LUMO localizations and Mulliken charges in target chromophores; see Figure S3 for complete listing of frontier molecular orbitals. All molecules are unsymmetrical and do not belong to any group of symmetry. Whereas the HOMO is centrally localized either on the diphenylamino or carbazole donors, the LUMO is spread over the adjacent 1,4-phenylene bridge. The Mulliken charges are localized accordingly, involving the donor moieties in **8** and mostly the π-conjugated bridge between the particular donor and acceptor.

The calculated dipole moments reflect the geometry with the out-of-plane orientation of both donor moieties (the torsion angle is about 50°). However, molecules in series **a** bearing more flexible diphenylamino group possess significantly higher ground state dipole moments of around 11 and 13 D as compared to carbazole derivatives **b** (Table 4).

The fundamental electronic absorption properties were investigated by TD-DFT method; the calculated positions of the longest-wavelength absorption maxima λ_{max}^{DFT} are gathered in Table 4, the spectra are provided in Figure S4. The calculated λ_{max}^{DFT} values correlate tightly with the experimental longest-wavelength absorption maxima measured in dichloromethane (Table 2) – see Figure S5. The spectra consist of two peaks; the low-energy peak corresponds to the HOMO→LUMO transition whereas the high-energy peak involves mostly the HOMO–2→LUMO and HOMO→LUMO+1 transitions. When comparing the corresponding pairs of chromophores, chromophores **8a**-**b** bearing 2,5-thienylene linker possess bathochromically shifted longest-wavelength absorption maxima. The same trend can be seen for chromophores **a** with *N*,*N*-diphenylamino donor, when compared to carbazole derivatives **b**.

First-order hyperpolarizabilities β were also calculated as shown in Table 4. The calculated β coefficients range from 85 to 373 × 10^{-30} esu. Correlations of the calculated β and experimental $\mu\beta$ or $\mu\beta_0$ products (EFISH experiment) are provided in Figures S5 and S6. Both correlations are very tight. In general, larger nonlinearities were calculated for chromophores **a**

with *N*,*N*-diphenylamino donor, the largest one belongs to chromophore **8a** with polarizable 2,5-thienylene π-linker.

2. Experimental section

General Information. All reagents and solvents were obtained from commercial sources and dried by using standard procedures before use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-500 and AVANCE-600 instruments using Me_4Si as an internal standard. IR spectra of samples (solid powders) were recorded on a Spectrum One Fourier transform IR spectrometer (Perkin Elmer) equipped with a diffuse reflectance attachment (DRA) in the frequency range 4000÷400 cm^{-1}. Spectrum processing and band intensity determination were carried out using the special software supplied with the spectrometer. Elemental analysis was carried on a Eurovector EA 3000 automated analyzer. Melting points were determined on Boetius combined heating stages and were not corrected. The chromatographic purification of compounds was achieved with silica gel Alfa Aesar 0.040-0.063 mm (230-400 mesh), eluting with CH_2Cl_2/hexane (1:2, v/v). The progress of reactions and the purity of compounds were checked by TLC on Sorbfil plates (Russia), in which the spots were visualized with UV light (λ 254 or 365 nm). The electrochemical studies of the compounds were performed with a home-designed 3-electrodes cell (WE: glassy carbon disk, RE: Ag wire, Ce: Pt). Ferrocene was added at the end of each experiment to determine redox potential values. UV Vis and fluorescence spectra were recorded with a Fluoromax-3 Jobin-Yvon Horiba spectrophotometer using standard 1 cm quartz cells. Compounds were excited at their absorption maxima (band of lowest energy) to record the emission spectra. The Φ_F values were calculated using a well-known procedure [18] with 9,10-*bis*(phenylethenyl)anthracene in cyclohexane (Φ_F = 1.00) as standard [19]. Experimental details on EFISH measurements are described elsewhere [20].

Synthesis of 5-(4-bromophenyl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (3). A mixture of 4′-Bromoacetophenone **1** (1.994 g, 10 mmol) and selenium dioxide (1.1 g, 10 mmol) in a solution of 1,4-dioxane (15 mL) and water (1 mL) was refluxed for 12 h. Selenium was filtered off,

washed with 1,4-dioxane (5 mL). The solvent was evaporated at reduced pressure. The residue was dissolved in a mixture of ethanol (5 mL) and acetic acid (5 mL), 3,4-diaminofurazan (**2**) (1.0 g, 10 mmol) was added, and the resulting mixture was refluxed for 1 h and cooled to room temperature. A precipitate formed was filtered, washed with ethanol, and dried in air. Compound **3** was obtained as a pale yellow solid. Yield 2.023 g (73 %), mp 159-160 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.80 (s, 1H), 8.38–8.33 (m, 2H), 7.91–7.86 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 158.7, 155.6, 152.2, 151.6, 133.4, 132.4, 130.9, 127.2. Calcd. for $C_{10}H_5BrN_4O$ (277.08): C, 43.35; H, 1.82; N, 20.22. Found: C, 43.37; H, 1.95; N, 20.20.

Synthesis of 5-(5-bromothiophen-2-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (5). *N*-Bromosuccinimide (4.45 g, 25 mmol) was added to a solution of 5-(1-benzothiophen-3-yl)pyrimidine (**4**) (2.04 g, 10 mmol) in DMF (15 ml). The obtained solution was stirred overnight at room temperature. The reaction mixture was diluted with water. The formed precipitate was filtered off, washed with water, dried, and recrystallized from ethanol. Yield 2.406 g (85%), orange solid, mp 213-215 °C. H NMR (500 MHz, DMSO-d_6) δ 9.73 (s, 1H), 8.40 (d, J = 4.1 Hz, 1H), 7.58 (d, J = 4.1 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.5, 153.5, 152.0, 151.5, 142.2, 135.4, 133.4, 122.9. Calcd. for $C_8H_3BrN_4OS$ (283.10): C, 33.94; H, 1.07; N, 19.79. Found: C, 33.90; H, 1.02; N, 19.55.

General procedure for the synthesis of 5-[4-(heteroaryl)phenyl]-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (7a,b) and 5-[5-(heteroaryl)thiophen-2-yl]-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (8a,b).

A mixture of 5-(4-bromophenyl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (**3**) (277 mg, 1.0 mmol) [or 5-(5-bromothiophen-2-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (**5**) (283 mg, 1.0 mmol)], corresponding arylboronic acid **6a,b** (1.2 mmol), $Pd(PPh_3)_4$ (115 mg, 10 mol %) and K_3PO_3 (530 mg, 2.5 mmol) was dissolved in 1,4-dioxane 15 mL. The reaction mixture was degassed and refluxed for 15 h under an argon atmosphere. After completion of the reaction (monitored by TLC), the reaction mixture was cooled, filtered, and dissolved in a mixture of EtOAc and water

(1:1, 50 mL), and the organic layer was separated. The aqueous layer was extracted with EtOAc (2 × 25 mL). The combined organic extracts were dried with $MgSO_4$ and the solvents evaporated. Purification by silica gel column chromatography with CH_2Cl_2/hexane (1:2, v/v) as an eluent to afford the title compounds (**7** and **8**).

4'-([1,2,5]Oxadiazolo[3,4-*b*]pyrazin-5-yl)-*N,N*-diphenyl-[1,1'-biphenyl]-4-amine (7a). Yield 375 mg (85%), dark violet solid, mp 223-224 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.87 (s, 1H), 8.54–8.47 (m, 2H), 7.99–7.94 (m, 2H), 7.81–7.76 (m, 2H), 7.39–7.35 (m, 4H), 7.14–7.10 (m, 6H), 7.08–7.05 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 159.4, 156.4, 152.9, 152.1, 148.4, 147.2, 144.3, 133.0, 132.1, 130.2, 128.5, 127.2, 125.2, 124.2, 122.9. ν (DRA, cm^{-1}) 3062 (w, C–H_{Ar}), 3053 (w, C–H_{Ar}), 3037(w, C–H_{Ar}), 1586 (s, C–C_A/C–N_{Ar}), 1561(s, C–C_{Ar}/C–N_{Ar}), 1488 (s, C–C_{Ar}/C–N_{Ar}), 1446 (s, C–C_{Ar}/C–N_{Ar}), 822 (s, C–H_{Ar}), 797 (s, C–H_{Ar}), 753 (s, C–H_{Ar}), 697 (s, C–H_{Ar}). Calcd. for $C_{28}H_{19}N_5O$ (441.49): C, 76.17; H, 4.34; N, 15.86. Found: C, 75.95; H, 4.32; N, 16.09.

5-(4'-(9*H*-Carbazol-9-yl)-[1,1'-biphenyl]-4-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (7b). Yield 338 mg (77%), red solid, mp 288-289 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.91 (s, 1H), 8.63–8.57 (m, 2H), 8.28 (dt, J = 7.8, 1.0 Hz, 2H), 8.20–8.11 (m, 4H), 7.84–7.78 (m, 2H), 7.53–7.45 (m, 4H), 7.33 (ddd, J = 7.9, 6.7, 1.3 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 159.5, 156.3, 152.9, 152.2, 143.9, 140.5, 138.1, 137.8, 134.0, 130.3, 129.3, 128.1, 127.7, 123.5, 121.1, 120.8, 110.2. ν (DRA, cm^{-1}) 3034 (w, C–H_{Ar}), 1564 (s, C–C_{Ar}/C–N_{Ar}), 1447 (s, C–C_{Ar}/ C–N_{Ar}), 746 (s, C–H_{Ar}), 723 (s, C–H_{Ar}). Calcd. for $C_{28}H_{17}N_5O$ (439.48): C, 76.52; H, 3.90; N, 15.94. Found: C, 76.65; H, 3.78; N, 16.10.

4-(5-([1,2,5]Oxadiazolo[3,4-*b*]pyrazin-5-yl)thiophen-2-yl)-*N,N*-diphenylaniline (8a). Yield 349 mg (78%), violet solid, mp 248-249 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.74 (s, 1H), 8.55 (d, J = 4.2 Hz, 1H), 7.81–7.74 (m, 2H), 7.72 (d, J = 4.2 Hz, 1H), 7.42–7.33 (m, 4H), 7.20–7.07 (m, 6H), 7.01–6.95 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 155.5, 154.5, 153.7, 152.8,

152.0, 149.2, 146.8, 139.0, 137.0, 130.3, 127.9, 125.9, 125.6, 125.5, 124.7, 121.9. ν (DRA, cm^{-1}) 3085 (w, C–H_{Ar}), 3062 (w, C–H_{Ar}), 3035 (w, C–H_{Ar}), 1589 (s, C–C_{Ar}/ C–N_{Ar}), 1568 (s, C–C_{Ar}/ C–N_{Ar}), 1488 (s, C–C_{Ar}/C–N_{Ar}), 1438 (s, C–C_{Ar}/C–N_{Ar}), 1405 (s, C–C_{Ar}/ C–N_{Ar}), 833 (s, C–H_{Ar}), 751 (s, C–H_{Ar}), 694 (s, C–H_{Ar}). Calcd. for $C_{26}H_{17}N_5OS$ (447.52): C, 69.78; H, 3.83; N, 15.65. Found: C, 69.83; H, 3.77; N, 15.67.

5-(5-(4-(9*H*-Carbazol-9-yl)phenyl)thiophen-2-yl)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine (8b). Yield 321 mg (72%), red solid, mp 246-248 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.82 (d, *J* = 2.1 Hz, 1H), 8.66 (dd, *J* = 4.0, 2.2 Hz, 1H), 8.28 (dt, *J* = 7.8, 1.1 Hz, 2H), 8.21 – 8.15 (m, 2H), 8.00 (dd, *J* = 4.0, 2.2 Hz, 1H), 7.83 – 7.78 (m, 2H), 7.54 – 7.44 (m, 4H), 7.33 (ddd, *J* = 7.9, 6.9, 1.2 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 155.4, 154.7, 152.7, 152.2, 152.1, 140.5, 140.3, 138.4, 136.8, 131.8, 128.4, 127.8, 127.3, 126.9, 123.5, 121.1, 120.9, 110.3. ν (DRA, cm^{-1}) 3093 (br. w, C–H_{Ar}), 3080 (br. w, C–H_{Ar}), 3060 (br. w, C–H_{Ar}), 3028 (br. w, C–H_{Ar}), 1599 (s, C–C_{Ar}/C–N_{Ar}), 1567 (s, C–C_{Ar}/ C–N_{Ar}), 1533 (s, C–C_{Ar}/ C–N_{Ar}), 1449 (s, C–C_{Ar}/ C–N_{Ar}), 1406 (s, C–C_{Ar}/ C–N_{Ar}), 837 (s, C–H_{Ar}), 749 (s, C–H_{Ar}), 724 (s, C–H_{Ar}). Calcd. for $C_{26}H_{15}N_5OS$ (445.50): C, 70.10; H, 3.39; N, 15.72. Found: C, 70.00; H, 3.54; N, 15.56.

Conclusion

In summary, four new push-pull chromophores bearing [1,2,5]oxadiazolo[3,4-*b*]pyrazine as electron-withdrawing part and amino group as donor were designed. There electrochemical and photophysical properties indicate that intense ICT occurs in these structures with electrochemical gap below 2.1 eV and strong emission solvatochromism. NLO responses were also measured by EFISH method. All experimental and theoretical results indicate a significant increase of ICT when the diphenylamino electro-donating group is used and when a 2,5-thienylene bridge is replacing the 1,4-phenylene linker. Compound **8a**, that combines these two characteristics, exhibits a particularly high figure of merit and appears as an interesting candidate for incorporation in a polymeric matrix to obtain a material with the high electro-optic coefficient.

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