Abstract: A series of novel V-shaped quinoxaline, [1,2,5]oxadiazolo[3,4-B]pyrazine and [1,2,5]thiadiazolo[3,4-B]pyrazine push–pull derivatives with 2,4′-biphenylene linker were designed and their electrochemical, photophysical and nonlinear optical properties were investigated. [1,2,5]Oxadiazolo[3,4-B]pyrazine is the stronger electron-withdrawing fragment as shown by electrochemical, and photophysical data. All compounds are emissive in a solid-state (from the cyan to red region of the spectrum) and quinoxaline derivatives are emissions in DCM solution. It has been found that quinoxaline derivatives demonstrate important solvatochromism and extra-large Stokes shifts, characteristic of twisted intramolecular charge transfer excited state as well as aggregation induced emission. The experimental conclusions have been justified by theoretical (TD-)DFT calculations.

Keywords: furazanopyrazine; [1,2,5]thiadiazolo[3,4-B]pyrazine; quinoxaline; donor–acceptor systems; twisted intramolecular charge transfer
Push–pull molecular materials have found applications as fluorescent sensors [7–10], dye-sensitized solar cells (DSSC) [11–14], nonfullerene organic photovoltaic (OPV) materials [15–17], and numerous other optoelectronic devices [18–21]. The intramolecular charge transfer (ICT) in push–pull molecular materials can be modulated either by playing on the A/D couple [1,2,22,23] or by changing the nature and length of the \( \pi \)-conjugated bridge [1,2,24,25]. In this context, \( \pi \)-deficient heterocycles are particularly interesting as A part, as follows: the electron-lone pairs of heteroatoms of the heterocyclic core can be indeed used for protonation, complexation, alkylation, or the formation of a hydrogen bond, modifying their electron-withdrawing character and tuning the optical properties of corresponding push–pull structures by redistribution of charge density [26–31].

1,2,5-Chalcogenadiazoles and their annulated derivatives have received great attention due to the remarkable combination of their interesting properties, synthesis, and applications in materials sciences [32–35]. Recently, some of us designed and demonstrated the possible applications of [1,2,5]oxadiazolo[3,4-\( b \)]pyrazine derivatives (also called furazanopyrazines) as effective multifunctional chemosensors (I) [36,37], charge-transport materials for photovoltaics (II) [38], and compounds with advanced nonlinear optical (NLO) properties (III) (Figure 2) [39].

Figure 1. Limiting resonance forms of p-nitroaniline, a typical push–pull structure.

Figure 2. Representative compounds bearing furazanopyrazine scaffold.

Phenylene bridges are typical linkers in push–pull structures, even if the aromaticity of the \( \pi \)-linker is directed toward the ICT [40,41]. The 1,4-phenylene unit is generally used, but the ortho arrangement can be interesting due to the steric hindrance that can lead to a twisted intramolecular charge transfer (TICT) excited state with large Stokes shifts [42,43].

This article is a further extension of our recent studies that are focused on the design of novel chromophores based on strong electron-withdrawing [1,2,5]oxadiazolo[3,4-\( b \)]pyrazine fragments [39]. Herein we report the synthesis of a new series of V-shaped D–\( \pi \)-A push–pull systems based on [1,2,5]oxadiazolo[3,4-\( b \)]pyrazine, [1,2,5]thiadiazolo[3,4-\( b \)]pyrazine, and quinoxaline acceptor cores and 2,4′-biphenylene \( \pi \)-linker. The systematic experimental investigation of their electronic and photophysical properties has been carried out, and these results were rationalized with the help of theoretical (TD)-DFT calculation.
2. Results and Discussion

2.1. Synthesis

The target V-shaped push–pull 5-(4’-(N,N-diphenylamino)-1,1’-biphenyl)-2-yl-[1,2,5]oxadiazolo[3,4-b]pyrazine (9a) and 5-(4’-(9-carbazol-9-yl)-1,1’-biphenyl)-2-yl-[1,2,5]oxadiazolo[3,4-b]pyrazine (9b) were prepared through two-step procedure according an early developed synthetic approach starting from commercially available 2’-bromoacetophenone (1) (Schemes 1 and 2) [39].

![Scheme 1. Synthesis of 5-(2-bromophenyl)-[1,2,5]oxadiazolo[3,4-b]pyrazine (5), 5-(2-bromophenyl)-[1,2,5]thiadiazolo[3,4-b]pyrazine (6), and 2-(2-bromophenyl)quinoxaline (7).](image1)

![Scheme 2. Synthesis and structure of V-shaped push–pull chromophores 9–11.](image2)

In order to study the effect of the electron-withdrawing part on photophysical and electrochemical properties of the push–pull system, [1,2,5]thiadiazolo[3,4-b]pyrazine (10a,b) and quinoxaline (11a,b) structural analogues were synthesized. In this case, 1,2,5-thiadiazole-3,4-diamine (3) and o-phenylenediamine (4) were initially used to obtain corresponding...
5-(2-bromophenyl)-[1,2,5]thiadiazolo[3,4-b]pyrazine (6) or 2-(2-bromophenyl)quinoxaline (7) with high yields (Scheme 1). All compounds were characterized by 1H/13C NMR and IR spectra as well as elemental analyses, and the results confirmed their structure.

In the second step, the desired chromophores 10a,b and 11a,b were obtained in good yields through the Suzuki–Miyaura cross-coupling reactions with the appropriate boronic acids 8a,b, as shown in Scheme 2.

2.2. Electrochemical Properties

Electrochemical behavior of compounds 9–11 were studied by cyclic voltammetry in dichloromethane (DCM) containing Bu4NPF6 electrolyte at a scan rate of 0.1 V/s. The working electrode was a glassy carbon disk. A 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. Representative CV diagrams of compounds are shown in Figure 3.

| Compounds | $E_{pa}$ [V] | $E_{1/2}^{red}$ [V] | $\Delta E$ [V] | $E_{HOMO}$ [eV] | $E_{LUMO}$ [eV] | $\lambda_{max}$ [nm] |
|-----------|--------------|---------------------|----------------|----------------|----------------|---------------------|
| 9a        | 0.79         | –1.24               | 2.04           | –5.59          | –3.56          | 608                 |
| 9b        | 1.08         | –1.20               | 2.28           | –5.88          | –3.60          | 544                 |
| 10a       | 0.72         | –1.50               | 2.22           | –5.52          | –3.30          | 569                 |
| 10b       | 0.87         | –1.55               | 2.42           | –5.67          | –3.25          | 513                 |
| 11a       | 0.74         | –2.44               | 3.17           | –5.54          | –2.36          | 391                 |
| 11b       | 1.10         | –2.36               | 3.46           | –5.90          | –2.44          | 359                 |

a All potentials are given versus Fc/Fc+. b $\Delta E = E_{pa} - E_{1/2}^{red}$. c $E_{HOMO/LUMO} = -(E_{ox1/red1} + 4.8)$. d Calculated $\lambda_{max}$ values ($\lambda = 1241/\Delta E$). e Irreversible peaks $E_p$. 

Figure 3. Cyclic voltamograms in DCM of compounds 9a (yellow), 10a (grey), and 11a (red) in negative (A) and positive (B) direction and of 9b (green), 10b (purple), and 11b (blue) in negative (C) and positive (D) direction.
Compounds 9b, 10b, and 11b bearing a 9H-carbazol-9-yl fragment as an electron-donating group exhibit a first irreversible oxidation process at, respectively, 1.08 V, 0.87 V, and 1.10 V vs. Fc/Fc⁺. The measured maximum current intensity is high in comparison with the values obtained for reduction processes, indicating a possible polymerization reaction on the electrode. As a consequence, an irreversible reduction broad peak is detected between −0.67 and −0.84 V on the reverse scan only after the oxidation of compounds (Figure S1). Upon initial scanning in the negative direction, a reversible reduction is observed at −0.95 and −1.10 V, respectively, for 9b and 10b, and an irreversible reduction is observed at $E_{pc} = −2.36$ V for 11b. When a donor is a diphenylamino group (compounds 9a, 10a, and 11a), the first irreversible oxidation is shifted towards lower potentials as compared to the respective carbazole analogues 9b, 10b, and 11b. This confirms the superior electron-donating strength of the diphenylamino moiety. For these compounds, the first oxidation is followed by a second one at a higher potential (Figure S2). The modification of the donor has a very weak influence on the reduction of the diazine (see Table 1 and Figure 3). These trends indicate a weak ground-state interaction between the donor and acceptor.

When comparing the reduction process of the electron-withdrawing fragments, the reduction potential increase in the following order 11 < 10 < 9, indicating that the [1,2,5] oxadiazolo[3,4-b]pyrazine electron-withdrawing fragment is the strongest one. As a result, compound 9a, bearing the strongest electron-donating and electron-withdrawing parts, showed the lowest electronic gap ($\Delta E$) and is expected to exhibit the most red-shifted absorption bands across the whole series. Compared to their 1,4-phenylene analogues previously described [39], compounds 9a and 9b exhibited a larger electronic gap (0.65 V and 0.48 V) due to more difficult both oxidation and reduction processes, which indicates a significantly lower ICT.

### 2.3. Photophysical Properties

The UV-Vis and photoluminescence (PL) spectra of compounds 9–11 were measured in DCM solution at room temperature and the data are reported in Table 2. The UV/Vis spectra are provided in Figure 4. Regarding the lowest energetic absorption band, as expected according to electrochemical studies, the diphenylamino derivatives exhibit red-shifted absorption compared to their carbazole analogues. Similarly, as far as the electron-withdrawing part is concerned, the absorption maxima increase in the following order: 11 < 10 < 9 in both the diphenylamino and carbazole series. Compounds 9 and 10 are not luminescent in DCM solution, whereas the quinoxaline derivatives 11a and 11b exhibited green and yellow emissions, respectively, with low quantum yield. The particularly large Stokes shifts (>12,000 cm⁻¹ for 11b) could indicate the presence of a TICT excited state.

**Table 2.** Photophysical data of compounds 9–11 in DCM solution and in KBr matrix.

| Compounds | DCM Solution | KBr Matrix |
|-----------|--------------|------------|
|           | $\lambda_{ab}$ [nm] (ε [mM⁻¹ cm⁻¹]) | $\lambda_{em}$ [nm] ($\Phi$ *) | Stoke Shift (cm⁻¹) | $\lambda_{em}$ [nm] |
| 9a        | 327 (23.0), 508 (3.3) | - a | - a | 755 |
| 9b        | 324 (13.4), 422 (2.3) | - a | - a | 636 |
| 10a       | 335 (23.2), 479 (3.1) | - a | - a | 662 |
| 10b       | 340 (16.8), 411sh (3.2) | - a | - a | 588 |
| 11a       | 311 (25.0), 374 (6.3) | 512 (0.03) | 7206 | 478 |
| 11b       | 326 (11.6), 340 (10.9) | 584 (0.01) | 12,288 | 464 |

* 9,10-diphenylethenylanthracene in cyclohexane as a standard ($\Phi_F = 1.00$).
In an effort to gain further insight into the photophysical process within push–pull derivatives 11, their emission spectra were registered in a series of aprotic solvents of increasing polarity. The positions of the corresponding emission maxima are reported in Table 3, and the normalized emission spectra registered for 11a, as well as a picture of the solution in the various solvents, can be seen in Figures 5 and 6 (the same data are presented for compound 11b in Figures S3 and S4). Whereas the position of the absorption maximum is not significantly affected by the polarity of the solvent, the position of the emission maxima is bathochromically shifted when the polarity of the solvent, which is estimated according to the Reichardt polarity scale [44], is increased. This pronounced positive emission solvatochromism is characteristic of ICT and is well documented for push–pull materials [45–48], in particular in the case of biphenylene linkers between A and D parts [49]. Large emission solvatochromism and low emission quantum yield in a polar solvent are characteristics of TICT [50,51].

Table 3. Emission solvatochromism of compounds 11.

| Compounds | λ_{em} [nm] \(^a\) |
|-----------|------------------|
|           | n-Heptane \(E_T(30) = 30.9\) \(^a\) | Toluene \(E_T(30) = 33.9\) \(^a\) | 1,4-Dioxane \(E_T(30) = 36.0\) \(^a\) | THF \(E_T(30) = 37.4\) \(^a\) | CHCl\(_3\) \(E_T(30) = 39.1\) \(^a\) | DCM \(E_T(30) = 40.7\) \(^a\) |
| 11a       | 456              | 487              | 521              | 534              | 573              | 584              |
| 11b       | 422              | 431              | 452              | 484              | 495              | 512              |

\(^a\) Reichardt polarity parameter (kcal mol\(^{-1}\)).
Aggregation-induced emission (AIE), a concept proposed by Tang and coworkers in 2001 [52,53], induces intensive emission in the solid-state of non- (or slightly) emissive chromophores in solution. A restriction of intramolecular motion is one of the mechanisms of AIE [53]. In order to study the potential AIE properties of compounds 11, their emission spectra were recorded in a mixture of MeCN and water of a different ratio (Figure 7 and Figure S5). The pictures of the solutions under UV irradiation are presented in Figure 8 and Figure S6. For 11a, no emission is observed in pure MeCN, while a dramatic increase in the emission intensity is observed when the water fraction is higher than 80%, inducing a new band centered at 519 nm. The highest intensity is observed for the water fraction of 97%. Compound 11b is slightly emissive in pure MeCN with a yellow emission centered at 570 nm. When the ratio of water is increased, an extinction of the emission is initially observed (a water fraction of 50/60%), followed by the appearance of a new, blue-shifted
emission band ($\lambda_{\text{max}} = 472$ nm) with the maximum intensity of 80% of water. For higher water fractions, the emission is slightly blue-shifted and lowered in intensity.

Figure 7. Left: Emission spectra of compound 11a in MeCN/water mixture ($c = 1.5 \times 10^{-5}$ M, $\lambda_{\text{exc}} = 374$ nm), right: emission intensity of 11a at emission maximum vs. water ration in MeCN/water mixture.

Figure 8. Fluorescence color of compound 11a in MeCN/water mixture (from left to right: 0%, 50%, 80%, 97% of water). The picture was taken in the dark upon irradiation with a handheld UV lamp ($\lambda_{\text{em}} = 366$ nm).

The compounds 9–11 are luminescent solids as measured in the KBr matrix. The emission maxima are listed in Table 2. The spectra and pictures of selected KBr pellets are presented in Figures 9 and 10. The KBr pellets exhibited intense emission from the blue for compound 11b to near-infrared for compound 9a. The emission is red-shifted in the same order as the emission bands recorded in solution.
Results of EFISH measurements for compounds 9–11 were subsequently calculated. All the calculated data are gathered in Table 5; see the ESI for further information.

2.4. NLO Properties

The second-order NLO properties of compounds 9–11 have been investigated in chloroform using the electric-field induced second harmonic generation (EFISH) method at a non-resonant incident wavelength of 1907 nm. The EFISH method provides an estimation of the NLO response as the scalar product between the permanent dipolar moment of the molecule and the vector component of, described as \( \beta \) [54–56]. The data are reported in Table 4. The NLO responses of compounds 9–11 are particularly low and we are close to the limit of detection of the system. It is therefore not reasonable to compare the values between them. For the 1,4-phenylene analogue of compounds 9a, a much higher \( \mu \beta \) value was measured \((700 \times 10^{-48} \text{ esu})\) [39]. This indicates that the 1,2-phenylene arrangement drastically reduces the NLO response due to the limited/diminished ICT.

![Normalized emission spectra of compounds 9–11 in KBr matrix (2 wt%).](image)

**Figure 9.** Normalized emission spectra of compounds 9–11 in KBr matrix (2 wt%).

![Emission color of KBr pellets doped with 2% of chromophores](image)

**Figure 10.** Emission color of KBr pellets doped with 2% of chromophores (from left to right: 9b, 10a, 10b, 11a, 11b). The picture was taken in the dark upon irradiation with a handheld UV lamp (\( \lambda_{\text{exc}} = 366 \text{ nm} \)).

| Compound | \( \mu \beta \) \((10^{-48} \text{ esu})\) |
|----------|------------------|
| 9a       | 80               |
| 9b       | 20               |
| 10a      | 80               |
| 10b      | 50               |
| 11a      | 40               |
| 11b      | 0                |

**Table 4.** Results of EFISH measurements for compounds 9–11.

2.5. Theoretical Calculation

Molecular structures and electronic properties of V-shaped push–pull chromophores 9–11 were theoretically investigated using the Gaussian 16 software package [57]. First, the geometries were optimized using the DFT B3LYP/6-311+G(2df,p) method in CHCl\(_3\). Using the same level of theory, the energies of the frontier molecular orbitals (HOMO/LUMO), ground-state dipole moments (\( \mu \)), and first hyperpolarizabilities (\( \beta \)) were subsequently calculated. All the calculated data are gathered in Table 5; see the ESI for further information.
The calculated values imply that both 1,4-phenylene moieties in 9–11. The optimized geometries of 9–11 are shown in Figure 11A. As can be seen, the central biphenylene π-linker, interconnecting the N,N-diphenylamino, and pyrazine-derived moieties, adopts twisted geometry with the central torsion angle between 20° and 60°. Carbazole derivatives b showed generally larger torsion angles. The heterocyclic moiety at position 2 is always turned out by about 45°, independently of the particular derivative. The bond length alternation of both 1,4-phenylene moieties of the π-linker was investigated, revealing the Bird index \( I_1 \) and the quinoid character (\( \delta r \)) within the range of 91–96/2–5% [58,59]. For unsubstituted benzene, the \( I_1 \) and \( \delta r \) are equal to 100 and 0, respectively. The calculated values imply that both 1,4-phenylene moieties in 9–11 are slightly polarized. Alternation of the heterocyclic acceptor significantly affected the ground state dipole moment of V-shaped chromophores. The largest ones were calculated for furazanopyrazine derivatives 9, while replacement of the fused terminal oxa/thiadiazolo fragment by benzene diminished the dipole moment significantly as seen for 11.

![Figure 11](image-url)  
*Figure 11. DFT-optimized geometries including Bird index/quinoid character of the particular 1,4-phenylene moieties (A) and HOMO (red) and LUMO (blue) localizations (B) in chromophores 9–11.*

The calculated energies of the frontier molecular orbitals (\( E_{\text{HOMO}}/E_{\text{LUMO}} \)) and their differences \( E \) are summarized in Table 5. The latter quantity correlates tightly with the electrochemical gaps (Figure S7). The oxadiazolopyrazine acceptor moiety in 9a–b im-

| Compounds | \( E_{\text{HOMO}}^{\text{DFT}} \) [eV] | \( E_{\text{LUMO}}^{\text{DFT}} \) [eV] | \( \Delta E_{\text{DFT}} \) [eV] | \( \mu \) [D] | \( \lambda_{\text{max}}^{\text{DFT}} \) [nm/eV] | \( \beta(-2\omega,\omega,\omega)_{\text{DFT}}^{\text{DFT}} \) [10^{-20} esu] |
|-----------|-----------------|-----------------|-----------------|------|-----------------|-----------------|
| 9a        | -5.49           | -3.45           | 2.04            | 8.11 | 447/2.77        | 504             |
| 9b        | -5.84           | -3.55           | 2.29            | 7.86 | 377/3.39        | 117             |
| 10a       | -5.43           | -3.26           | 2.17            | 4.24 | 420/2.95        | 311             |
| 10b       | -5.81           | -3.34           | 2.47            | 4.30 | 357/3.47        | 74              |
| 11a       | -5.36           | -2.33           | 3.03            | 0.87 | 335/3.70        | 53              |
| 11b       | -5.77           | -2.40           | 3.37            | 2.37 | 301/4.12        | 18              |

All data calculated at the DFT level by using the Gaussian® 16 software package and DFT B3LYP/6-311+G(2df,p) method in CHCl₃. The first hyperpolarizabilities \( \beta(-2\omega,\omega,\omega) \) were calculated at 1907 nm. The electronic absorption spectra, the longest-wavelength absorption maxima and the corresponding electron transitions were calculated using TD-DFT (\( n_{\text{states}} = 8 \)) B3LYP/6-311+G(2df,p).
parts the strongest ICT with the lowest calculated HOMO–LUMO gaps as compared to chromophores 10 and 11. When comparing the triads of chromophores a and b, N,N-diphenylamino-substituted derivatives a possess lower HOMO–LUMO gaps than the corresponding carbazole derivatives b. Figure 9B shows HOMO and LUMO localizations in the particular derivatives; an obvious charge-separation is seen for 9a and 9b. For N,N-diphenylamino-substituted derivatives 10a and 11a are the situation similar, which is in contrast to carbazoles 10b and 11b. In these derivatives, both HOMO and LUMO are predominantly cumulated over the carbazole’s nitrogen atom, which results in their diminished ICT character and larger ∆E values.

Fundamental optical properties of 9–11 were investigated by TD-DFT CAM-B3LYP/6-311+G(2df,p) (nstates = 8) method. The calculated electronic absorption spectra along with the experimental ones are visualized in Figure S8. Both spectra feature the same shape and number of peaks and mostly differ in the position of the longest-wavelength absorption maxima. The λmax values listed in Table 5 showed a very tight correlation with the experimental ones (Table 1)—see Figure S9. According to the aforementioned discussion on the HOMO–LUMO gap, oxadiazolopyrazine chromophores 9a–b possess the most bathochromically shifted absorption maxima. Hence, both O→S replacement and fusing of benzene rings as in 10 and 11 shift the absorption maxima hypsochromically. An inspection of the transition forming the particular bands revealed that the longest wavelength absorption bands of chromophores 9a–b, 10a, and 11a are generated by the HOMO→LUMO transition and these can be designed as CT bands. The corresponding high-energy bands (blue shifted) involve also the HOMO–1→LUMO and the HOMO→LUMO+1 transitions. On the contrary, the absorption of chromophores 10b and 11b is dominated by the HOMO–2→LUMO transition, with a weak contribution of the HOMO→LUMO transition seen for 10b. These observations agree with their largest HOMO–LUMO gaps and the most hypsochromically shifted spectra.

The first order hyperpolarizability β(–2ω, ω, ω) calculated at 1907 nm is listed in Table 5. As can be seen, the largest polarizabilities were calculated for chromophores 9a and 10a, similarly to the EFISH experiment. Oxadiazolopyrazine, or eventually thiadiazolopyrazine, in combination with an N,N-diphenylamino substituent, is the most useful electron acceptor/donor pair in V-shaped NLOphores 9–11.

3. Experimental Methods

3.1. General Information

All reagents and solvents were obtained from commercial sources and dried by using standard procedures before use. Starting materials 5 and 7 were prepared according to the earlier reported procedure [60]. The 1H and 13C NMR spectra were recorded on a Bruker AVANCE-600 instruments using Me4Si as an internal standard. 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 CH2Cl2/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). IR spectra of samples (solid powders) were recorded on a Spectrum One Fourier transform IR spectrometer (Perkin Elmer, Waltham, MA, USA) 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.

3.2. Electrochemical Characterization

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.
3.3. Photophysical Characterization

The absorption spectra of the samples were detected with a JASCO V-650 instrument, whereas the emission spectra were detected by a Horiba Fluoromax spectrophotometer. UV/Vis and fluorescence spectra were recorded by using standard 1 cm quartz cells. Compounds were excited at their absorption maxima in solution (band of lowest energy) to record the emission spectra. The Φ<sub>e</sub> values were calculated by using a well-known procedure with 9,10-diphenylethynylanthracene in cyclohexane as a standard (Φ<sub>e</sub> = 1.00) [61]. Stokes shifts were calculated by considering the lowest energy absorption band. Experimental details on EFISH measurements are described elsewhere [62].

**Synthesis of 5-(2-bromophenyl)-[1,2,5]thiadiazolo[3,4-b]pyrazine (6).** A mixture of 2'-bromoacetophenone (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 and 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), washed with ethanol, and dried in air. Compound 6 was obtained as a pale-yellow solid. Yield 2.2 g (75%), mp 169–170 °C. The 1H NMR (600 MHz, DMSO-<sup>d6</sup>) δ 9.45 (s, 1H), 7.90 (dd, <i>J</i> = 8.1, 1.1 Hz, 1H), 7.79 (ddd, <i>J</i> = 7.6, 1.7 Hz, 1H), 7.66 (td, <i>J</i> = 7.5, 1.1 Hz, 1H), 7.57 (td, <i>J</i> = 7.7, 1.7 Hz, 1H). The 13C NMR (151 MHz, DMSO-<sup>d6</sup>) δ 158.2, 154.0, 153.4, 151.7, 137.3, 133.7, 132.8, 132.7, 128.9, 121.7. Calcd. For C<sub>13</sub>H<sub>9</sub>BrN<sub>4</sub>O (293.14): C, 40.97; H, 1.72; N, 19.11. Found: C, 41.02; H, 1.77; N, 19.16.

**General procedure for the synthesis of 5-(4′-(heteroaryl)-[1,1′-biphenyl]-2-yl)-[1,2,5] oxadiazolo[3,4-b]pyrazine (9), 5-(4′-(heteroaryl)-[1,1′-biphenyl]-2-yl)-[1,2,5]thiadiazolo[3,4-b] pyrazine (10), and 2-(4′-(heteroaryl)-[1,1′-biphenyl]-2-yl)-quinoxaline (11).** A mixture of 5-(2-bromophenyl)-[1,2,5]oxadiazolo[3,4-b]pyrazine (5) (277 mg, 1.0 mmol), 5-(2-bromophenyl)-[1,2,5]thiadiazolo[3,4-b]pyrazine (6) (293 mg, 1.0 mmol) or 2-(2-bromophenyl)quinoxaline (7) (285 mg, 1.0 mmol), corresponding arylboronic acid 8a or 8b (1.2 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (115 mg, 10 mol %) and K<sub>2</sub>PO<sub>3</sub> (530 mg, 2.5 mmol) were dissolved in 1,4-dioxane (15 mL). The reaction mixture was cooled, filtered, and dissolved in a mixture of EtOAc and water (1:1, 50 mL). The organic layer was separated, the aqueous layer was extracted with EtOAc (2 × 25 mL), the combined organic extracts were dried with MgSO<sub>4</sub> and the solvents were evaporated. Purification by silica gel column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:2, v/v) as an eluent afforded the title compounds 9–11.

**2′-([1,2,5]Oxadiazolo[3,4-b]pyrazin-5-yl)-N,N-diphenyl-[1,1′-biphenyl]-4-amine (9a).** Yield 348 mg (79%), dark violet solid, mp 160–161 °C. The 1H NMR (600 MHz, DMSO-<sup>d6</sup>) δ 8.31 (s, 1H), 7.91 (d, <i>J</i> = 7.7 Hz, 1H), 7.76 (t, <i>J</i> = 7.5 Hz, 1H), 7.69–7.63 (m, 2H), 7.32 (t, <i>J</i> = 7.7 Hz, 4H), 7.17 (d, <i>J</i> = 8.2 Hz, 2H), 7.10–7.04 (m, 6H), 6.91 (d, <i>J</i> = 8.2 Hz, 2H). The 13C NMR (151 MHz, DMSO-<sup>d6</sup>) δ 164.5, 157.3, 152.8, 151.3, 148.0, 147.1, 141.4, 134.4, 133.2, 132.5, 131.8, 131.6, 130.5, 130.1, 128.5, 125.1, 124.2, 122.8. Calcd. for C<sub>28</sub>H<sub>15</sub>N<sub>5</sub>O (441.49): C, 76.17; H, 4.34; N, 15.86. Found: C, 76.24; H, 4.46; N, 15.70. Φ<sub>e</sub> (DRA, cm<sup>−1</sup>) 3061 (w, C–H<sub>Ar</sub>) 3036 (w, C–H<sub>Ar</sub>), 1588 (s, C–C<sub>Ar</sub>/C–N<sub>Ar</sub>), 1487 (s, C–C<sub>Ar</sub>/C–N<sub>Ar</sub>), 1443 (s, C–C<sub>Ar</sub>/C–N<sub>Ar</sub>), 753 (s, C–H<sub>Ar</sub>), 695 (s, C–H<sub>Ar</sub>)

**5-(4′-(9H-Carbazol-9-yl)-[1,1′-biphenyl]-2-yl)-[1,2,5]oxadiazolo[3,4-b]pyrazine (9b).** Yield 311 mg (71%), red-orange solid, mp 226–227 °C. The 1H NMR (600 MHz, DMSO-<sup>d6</sup>) δ 8.50 (s, 1H), 8.26 (dt, <i>J</i> = 7.8, 0.9 Hz, 2H), 8.00 (dd, <i>J</i> = 7.7, 1.2 Hz, 1H), 7.88–7.82 (m, 2H), 7.75 (dd, <i>J</i> = 7.7, 6.9, 1.8 Hz, 1H), 7.65–7.62 (m, 2H), 7.60–7.56 (m, 2H), 7.46 (dd, <i>J</i> = 8.3, 7.1, 1.2 Hz, 2H), 7.38 (dt, <i>J</i> = 8.2, 0.9 Hz, 2H), 7.31 (dd, <i>J</i> = 7.9, 7.1, 1.0 Hz, 2H). The 13C NMR (151 MHz, DMSO-<sup>d6</sup>) δ 164.2, 157.3, 152.9, 151.4, 141.0, 140.4, 138.6, 137.3, 134.8, 132.7, 132.3, 132.1, 131.0, 129.2, 127.6, 126.8, 123.4, 121.1, 120.8, 110.0. Calcd. for C<sub>20</sub>H<sub>17</sub>N<sub>5</sub>O (439.48): C, 76.52; H, 3.90; N, 15.94. Found: C, 76.47; H, 3.78; N, 15.82. Φ<sub>e</sub> (DRA, cm<sup>−1</sup>) 3060 (w, C–H<sub>Ar</sub>) 1600 (s, C–C<sub>Ar</sub>/C–N<sub>Ar</sub>), 1450 (s, C–C<sub>Ar</sub>/C–N<sub>Ar</sub>), 749 (s, C–H<sub>Ar</sub>) 724 (s, C–H<sub>Ar</sub>)}
2′-[(1,2,5)Thiadiazolo[3,4-b]pyrazin-5-yl]-N,N-diphenyl-[1,1′-biphenyl]-4-amine (10a).
Yield 278 mg (61%), bright orange solid, mp 189–190 °C. The 1H NMR (600 MHz, DMSO-d6) δ 8.48 (s, 1H), 7.89 (dd, J = 7.7, 1.3 Hz, 1H), 7.71 (td, J = 7.5, 1.4 Hz, 1H), 7.63 (dd, J = 14.9, 7.6, 1.3 Hz, 2H), 7.34–7.29 (m, 4H), 7.13–7.09 (m, 2H), 7.08–7.04 (m, 2H), 7.04–7.00 (m, 4H), 6.89–6.85 (m, 2H). The 13C NMR (151 MHz, DMSO-d6) δ 159.9, 154.5, 152.8, 152.1, 147.5, 147.2, 142.2, 135.1, 133.5 131.7, 131.5, 131.0, 124.8, 124.9, 124.0, 123.0. Calcd. for C28H25N5S (457.56): C, 73.50; H, 4.19; N, 15.37. Found: C, 73.70; H, 4.24; N, 15.21. ν (DRA, cm−1) 3085 (w, C–HAr), 3064 (w, C–HAr), 3025 (w, C–HAr), 1594 (s, C–CA/C–NAr), 1483 (s, C–CA/C–NAr), 754 (s, C–HAr), 693 (s, C–HAr).

5-[4′-(9H-Carbazol-9-yl)-[1,1′-biphenyl]-2-yl]-[1,2,5]thiadiazolo[3,4-b]pyrazine (10b).
Yield 268 mg (59%), yellow solid, mp 250–251 °C. The 1H NMR (600 MHz, DMSO-d6) δ 8.65 (s, 1H), 8.24 (d, J = 7.8 Hz, 2H), 7.98 (d, J = 7.6 Hz, 1H), 7.80 (q, J = 5.1, 4.2 Hz, 2H), 7.73 (td, J = 6.8, 5.7, 2.9 Hz, 1H), 7.61–7.48 (m, 4H), 7.44 (t, J = 7.6 Hz, 2H), 7.36–7.25 (m, 4H). The 13C NMR (151 MHz, DMSO-d6) δ 159.5, 154.5, 152.9, 152.0, 140.8, 140.4, 139.2, 136.8, 135.4, 132.1, 132.0, 131.7, 131.0, 129.1, 127.4, 126.7, 123.3, 121.1, 120.7, 110.0. Calcd. for C28H23N5S (455.54): C, 73.83; H, 3.76; N, 15.37. Found: C, 73.70; H, 3.75; N, 15.24. ν (DRA, cm−1) 3060 (w, C–HAr), 3042 (w, C–HAr), 1597 (s, C–CA/C–NAr), 1452 (s, C–CA/C–NAr), 751 (s, C–HAr), 725 (s, C–HAr).

N,N-Diphenyl-2′-(quinolin-2-yl)-[1,1′-biphenyl]-4-amine (11a).
Yield 332 mg (74%), pale yellow solid, mp 135–137 °C. The 1H NMR (600 MHz, DMSO-d6) δ 8.41 (s, 1H), 8.07 (dd, J = 8.5, 7.1, 1.6 Hz, 2H), 7.89–7.82 (m, 3H), 7.63 (td, J = 7.1, 6.6, 1.5 Hz, 1H), 7.60–7.55 (m, 2H), 7.30–7.23 (m, 4H), 7.02 (dd, J = 7.9, 5.9 Hz, 4H), 6.99–6.95 (m, 4H), 6.86–6.80 (m, 2H). The 13C NMR (151 MHz, DMSO-d6) δ 154.9, 147.3, 147.0, 146.9, 142.1, 140.9, 140.4, 134.6, 134.6, 131.4, 131.0, 130.5, 130.4, 130.3, 130.0, 129.5, 129.3, 128.3, 124.4, 123.7, 123.4. Calcd. for C23H22N4 (449.56): C, 85.50; H, 5.16; N, 9.35. Found: C, 85.49; H, 5.36; N, 9.29. ν (DRA, cm−1) 3057 (w, C–HAr), 3042 (w, C–HAr), 1585 (s, C–CA/C–NAr), 1492 (s, C–CA/C–NAr), 1481 (s, C–CA/C–NAr), 752 (s, C–HAr), 694 (s, C–HAr).

9-(2′-(Quinoxalin-2-yl)-[1,1′-biphenyl]-4-yl)-9H-carbazole (11b).
Yield 379 mg (85%), pale yellow solid, mp 158–159 °C. The 1H NMR (600 MHz, DMSO-d6) δ 8.56 (s, 1H), 8.25–8.21 (m, 2H), 8.08 (td, J = 8.5, 1.7 Hz, 2H), 7.93 (dd, J = 7.4, 1.1 Hz, 1H), 7.90–7.84 (m, 2H), 7.75–7.71 (m, 2H), 7.70–7.66 (m, 1H), 7.52–7.49 (m, 2H), 7.41 (dd, J = 8.9, 7.3 Hz, 4H), 7.31–7.26 (m, 4H). The 13C NMR (151 MHz, DMSO-d6) δ 154.6, 146.9, 142.1, 140.6, 140.5, 140.5, 139.9, 136.7, 136.4, 131.8, 131.5, 130.9, 130.8, 130.6, 130.5, 129.6, 129.3, 128.9, 127.2, 126.7, 123.2, 121.0, 120.6, 109.9. Calcd. for C23H19N3 (447.54): C, 85.88; H, 4.73; N, 9.39. Found: C, 85.95; H, 4.85; N, 9.41. ν (DRA, cm−1) 3055 (w, C–HAr), 3042 (w, C–HAr), 1598 (s, C–CA/C–NAr), 1450 (s, C–CA/C–NAr), 748 (s, C–HAr), 724 (s, C–HAr).

4. Conclusions
In summary, we have designed a series of push–pull chromophores bearing quinoxaline, [1,2,5]oxadiazolo[3,4-b]pyrazine, and [1,2,5]thiadiazolo[3,4-b]pyrazine as A part and 2,4′-biphenylene as a π-conjugated linker. The [1,2,5]oxadiazolo[3,4-b]pyrazine fragment appears as the strongest A part according to experimental electrochemical and photophysical results and theoretical calculation. With regards to 4,4′-biphenylene and 1,4-phenylene-2,5-thiénylene known analogues, these compounds exhibit reduced ICT leading to a low NLO response. Nevertheless, all compounds exhibited intense emissions in the solid state ranging from cyan to red/near-infrared. Quinoxaline derivatives exhibited TICT emission with intense solvatochromism, large Stokes shifts, and AIE.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27134250/s1, Figures S1 and S2: Oxidation study of compounds 9b, 10b, 11a, and 11b Figure S3: Normalized emission spectra of compound 11b in a series of aprotic solvents. Figure S4: Fluorescence color change experienced by 11b in various solvents. Figure S5: Emission spectra of compound 11b in MeCN/water mixture. Figure S6: Fluorescence color of compound 11b in MeCN/water mixture. Figure S7: A correlation of the experimental (ELCH) and DFT-calculated HOMO–LUMO gaps of chromophores 9–11. Figure S8: TD-DFT (nstates = 8)
References

1. Bureš, F. Fundamental aspects of property tuning in push-pull molecules. RSC Adv. 2014, 4, 58826–58851. [CrossRef]
2. Beverina, L.; Pagani, G.A. π-Conjugated zwitterions as paradigm of donor-acceptor building blocks in organic-based materials. Acc. Chem. Res. 2014, 47, 319–329. [CrossRef] [PubMed]
3. Kivala, M.; Diederich, F. Acetylene-derived strong organic acceptors for planar and nonplanar push-pull chromophores. Acc. Chem. Res. 2009, 42, 235–248. [CrossRef] [PubMed]
4. Kato, S.; Diederich, F. Non-planar push-pull chromophores. Chem. Commun. 2010, 46, 1994–2006. [CrossRef]
5. Meier, H. Conjugated oligomers with terminal donor-acceptor. Angew. Chem. Int. Ed. 2005, 44, 2482–2506. [CrossRef]
6. Kivala, M.; Diederich, F. Conjugation and optoelectronic properties of acetylenic scaffolds and charge-transfer chromophores. Pure Appl. Chem. 2008, 80, 411–427. [CrossRef]
7. Ipuy, M.; Billon, C.; Micouin, G.; Samarut, J.; Andraud, C.; Bretonniere, Y. Fluorescent push-pull responsive probes for ratiometric detection of intracellular pH. Org. Biomol. Chem. 2014, 2, 3641–3648. [CrossRef]
8. Lee, S.-C.; Heo, J.; Woo, H.C.; Lee, J.-A.; Seo, Y.H.; Lee, C.-L.; Kim, S.; Kwon, O.-P. Fluorescent molecular rotors for viscosity. Chem.-Eur. J. 2018, 24, 13706–13718. [CrossRef]
9. Lee, S.; Kim, S.-H.; Lee, S.; Lee, Y.; Lee, S.; Yang, K.-H.; Wang, K.-K.; Han, W.-S. Pyridazine-carbazole based fluorescent probes for volatile acid detection. Dyes Pigment. 2021, 194, 106913.
10. Dal Molin, M.; Verolet, Q.; Soleimanpour, S.; Matile, S. Mechanosensitive membrane probes. Chem.-Eur. J. 2015, 21, 6012–6021. [CrossRef]
11. Ji, J.M.; Zhou, H.; Kim, H.K. Rational design criteria for D-π-A structured organic and porphyrin sensitizers for highly efficient dyes-sensitized solar cells. J. Mater. Chem. A 2018, 6, 14518–14545. [CrossRef]
12. Lu, J.; Liu, S.; Wang, M. Push-pull zinc porphyrins as light-harvesters for efficient dye sensitized solar cells. Front. Chem. 2018, 6, 541. [CrossRef] [PubMed]
13. Yella, A.; Mai, C.-L.; Zakeeruddin, S.M.; Chang, S.N.; Hsieh, C.-H.; Yeh, C.-Y.; Graetzel, M. Molecular engineering of push-pull porphyrin dyes for highly efficient dye-sensitized solar cells: The role of benzene spacers. Angew. Chem. Int. Ed. 2014, 53, 2973–2977. [CrossRef]
14. Verbitskiy, E.V.; Rusinov, G.L.; Chupakhin, O.N.; Charushin, V.N. Azines as unconventional anchoring groups for dye-sensitized solar cells. The first decade of research advances and future outlook. Dyes Pigment. 2021, 194, 109650. [CrossRef]
15. Li, W.; Ye, L.; Li, S.; Yao, H.; Ade, H.; Hou, J. A high-efficiency organic solar cell enabled by the strong intramolecular electron push-pull effect of the nonfullerene acceptor. Adv. Mater. 2018, 30, 1707170. [CrossRef] [PubMed]
16. Du, S.; Yao, N.; Liu, S.; Xu, Y.; Cao, J.; Zhuang, W.; Yu, J.; Wang, N.; Yu, D.; Zhang, F.; et al. Nonfullerene acceptors from thieno[3,2-b]thiophene-fused naphthalene-donor with six-member-ring connection for efficient organic solar cells. Dyes Pigment. 2021, 185, 108892. [CrossRef]
17. Simón Marquéz, P.; Castán, J.M.A.; Raul, B.A.L.; Londi, G.; Ramirez, I.; Pshenichkov, M.S.; Beljonne, D.; Walzer, K.; Blais, M.; Allain, M.; et al. Triphenylamine/tetracyclobutadiene-based π-conjugated push-pull molecules end-capped with arene platforms: Synthesis, photophysics, and photovoltaic response. Chem.-Eur. J. 2020, 26, 16422–16433. [CrossRef] [PubMed]
18. Ostroverkhova, O. Organic Optoelectronic Materials: Mechanisms and Applications. Chem. Rev. 2016, 116, 13279–13412. [CrossRef]
19. Payne, A.-J.; Rice, N.A.; McAfee, S.M.; Lo, S.; Josse, P.; Cabanetos, P.; Rishko, C.; Lessard, B.H.; Welch, G.C. Donor or Acceptor? How selection of the rylene imide end cap impacts the polarity of π-conjugated molecules for organic electronics. ACS Appl. Energy Mater. 2019, 1, 4906–4916. [CrossRef]
20. Liu, J.; Ouyang, C.; He, W.; Cao, A. Progress in the enhancement of electro-optic coefficients and orientation stability for organic second-order nonlinear optical materials. *Dyes Pigment.* **2020**, *181*, 108509. [CrossRef]

21. Wong, M.Y.; Zysman-Colman, E. Purely organic thermally activated delayed fluorescence materials for organic light-emitting diodes. *Adv. Mater.* **2017**, *29*, 1605444. [CrossRef] [PubMed]

22. Moreno-Yruela, C.; Garin, J.; Orduna, J.; Franco, S.; Quintero, E.; López-Navarrete, J.T.; Diosdado, B.E.; Villacampa, B.; Casado, J.; Andreu, R. D-N-A compounds with tunable intramolecular charge transfer achieved by incorporation of bitenolide nitriles as acceptor moieties. *J. Org. Chem.* **2015**, *80*, 12115–12128. [CrossRef]

23. Tydlitá, J.; Fecková, M.; Le Poul, P.; Pytela, O.; Klikar, M.; Rodríguez-López, J.; Robin-le Guen, F.; Achelle, S. Influence of donor-substituents on triphenylenes chromophores bearing pyridine fragments. *Eur. J. Org. Chem.* **2019**, *2019*, 1921–1930. [CrossRef]

24. Klikar, M.; Bureš, F.; Pytela, O.; Mikysek, T.; Padělková, Z.; Barsella, A.; Dorkenoo, K.; Achelle, S. N,N′-Dibutylbarbituric acid as an acceptor moiety in push-pull chromophores. *New J. Chem.* **2013**, *37*, 4230–4240. [CrossRef]

25. Stefko, M.; Tzirakis, M.D.; Breiten, B.; Ebert, M.O.; Dumele, O.; Schweizer, W.B.; Gisselbrecht, J.P.; Boudon, C.; Beels, M.T.; Biaggio, I.; et al. Donor-acceptor (D-A)-substituted polyyne chromophores: Modulation of their optoelectronic properties by varying the length of the acetylene spacer. *Chem.-Eur. J.* **2013**, *19*, 12693–12704. [CrossRef]

26. Achelle, S.; Rodríguez-López, J.E.; Robin-Le Guen, F. Photoluminescence properties of Aryl-, Arylvinyl-, and arylethynylpyrimidine derivatives. *ChemistrySelect* **2018**, *3*, 1852–1886. [CrossRef]

27. Meti, P.; Park, H.-H.; Gong, Y.-D. Recent developments in pyrazine functionalized pi-conjugated materials for optoelectronic applications. *J. Mater. Chem. C* **2020**, *8*, 352–379. [CrossRef]

28. Nosova, E.V.; Achelle, S.; Lipunova, G.N.; Charushin, V.N.; Chupakhin, O.N. Functionalized benzazines as luminescent materials and component for optoelectronics. *Russ. Chem. Rev.* **2019**, *88*, 1128–1178. [CrossRef]

29. Verbitskiy, E.V.; Rusinov, G.L.; Chupakhin, O.N.; Charushin, V.N. Design of fluorescent sensors based on azaheterocyclic push-pull systems towards nitroaromatic explosives and related compounds: Review. *Dyes Pigment.* **2020**, *180*, 108141. [CrossRef]

30. Fecková, M.; Le Poul, P.; Bureš, F.; Robin-le Guen, F.; Achelle, S. Nonlinear optical properties of pyrimidine chromophores. *Dyes Pigment.* **2020**, *182*, 108659. [CrossRef]

31. Gupta, S.; Milton, M.D. Design and synthesis of novel V-shaped AIEE active quinoxalines for acidochromic applications. *Dyes Pigment.* **2019**, *165*, 474–487. [CrossRef]

32. Rakitin, O.A.; Zibarev, A.V. Synthesis and Applications of 5-Membered Halogen-Nitrogen π-Heterocycles with Three Heteroatoms. *Asian J. Org. Chem.* **2018**, *7*, 2397–2416. [CrossRef]

33. Konstantinova, L.S.; Rakitin, O.A. Chalcogen exchange in chalcogen–nitrogen π-heterocycles. *Mendelev Commun.* **2021**, *31*, 433–441. [CrossRef]

34. Sheremetev, A.B.; Yudin, I.L. Advances in the chemistry of furazano[3,4-b]pyrazines and their analogues. *Russ. Chem. Rev.* **2003**, *72*, 87–100. [CrossRef]

35. Makhova, N.N.; Belen’kii, L.I.; Gaziieva, G.A.; Dalinger, I.L.; Konstantinova, L.S.; Kuznetsov, V.V.; Kravchenko, A.N.; Krayushkin, M.M.; Rakitin, O.A.; Starosotnikov, A.M.; et al. Progress in the chemistry of nitrogen-, oxygen- and sulfur-containing heterocyclic systems. *Russ. Chem. Rev.* **2020**, *89*, 55–124. [CrossRef]

36. Verbitskiy, E.V.; Kvashnin, Y.A.; Baranova, A.A.; Yakovleva, Y.A.; Khokhlov, K.O.; Rusinov, G.L.; Charushin, V.N. 9-Ethyl-3-[6-(het)aryl]-[1,2,5]oxadiazolo[3,4-b]pyrazin-5-yl)-9H-carbazoles: Synthesis and study of sensitivity to nitroaromatic compounds. *Russ. Chem. Bull.* **2018**, *67*, 1078–1082. [CrossRef]

37. Verbitskiy, E.V.; Kvashnin, Y.A.; Baranova, A.A.; Khokhlov, K.O.; Chuvashov, R.D.; Yakovleva, Y.A.; Makarova, N.I.; Vetrova, E.V.; Metelitsa, A.V.; Rusinov, G.L.; et al. Novel fluorophores based on imidazopyrazine derivatives: Synthesis and photophysical characterization focusing on solvatochromism and sensitivity towards nitroaromatic compounds. *Dyes Pigment.* **2019**, *168*, 248–256. [CrossRef]

38. Kvashnin, Y.A.; Verbitskiy, E.V.; Eltsov, O.S.; Slepukhin, P.A.; Tameev, A.R.; Nekrasova, N.V.; Rusinov, G.L.; Nunzi, J.-M.; Chupakhin, O.N.; Charushin, V.N. Dibenzo[bf]furazano[3,4-b]quinoxalines: Synthesis by intramolecular cyclization through direct transition metal-free C–H functionalization and electrochemical, photophysical, and charge mobility characterization. *ACS Omega* **2020**, *5*, 8200–8210. [CrossRef]

39. Verbitskiy, E.V.; Achelle, S.; Bureš, F.; Le Poul, P.; Barsella, A.; Kvashnin, Y.A.; Rusinov, G.L.; Robin-le Guen, F.; Chupakhin, O.N.; Charushin, V.N. Synthesis, photophysical and nonlinear optical properties of [1,2,5]oxadiazolo[3,4-b]pyrazine-based linear push-pull systems. *J. Photochem. Photobiol. A Chem.* **2021**, *404*, 112900. [CrossRef]

40. Kůlnáhková, J.; Bureš, F.; Opršal, J.; Kuznik, W.; Mikysek, T.; Růžička, A. 1,4-phenylene and 2,5-thienylene π-linkers in charge-transfer chromophores. *Asian J. Org. Chem.* **2013**, *2*, 422–431. [CrossRef]

41. Marco, A.B.; Burrezo, P.M.; Mosteo, L.; Franco, S.; Garin, J.; Orduna, J.; Diosdado, B.E.; Villacampa, B.; Lopez Navarrete, J.T.; Casado, J.; et al. Polarization, second order nonlinear optical properties and electrochromism in 4H-pyrylidene chromophores with quinoid/aromatic thiophene ring bridge. *RSC Adv.* **2015**, *5*, 231–242. [CrossRef]

42. He, J.; Mathew, S.M.; Cornett, S.D.; Grundy, S.C.; Hartley, C.S. Ortho-phenylene oligomers with terminal push-pull substitution. *Org. Biomol. Chem.* **2012**, *10*, 3398–3405. [CrossRef]

43. Hammer, B.A.G.; Müller, K. Dimensional evolution of polyphenylenes: Expanding in all directions. *Chem. Rev.* **2016**, *116*, 2103–2140. [CrossRef] [PubMed]
44. Reichardt, C. Solvatochromic dyes as solvent polarity indicators. *Chem. Rev.* 1994, 94, 2319–2358. [CrossRef]
45. Lartia, R.; Allain, C.; Bordeau, G.; Schmidt, F.; Fiorini-Desbuisschert, C.; Charra, F.; Teulade Fichou, M.-P. Synthetic strategies to derivatizable triphenylamine displaying high two-photon absorption. *J. Org. Chem.* 2008, 73, 1732–1744. [CrossRef]
46. Katan, C.; Charlot, M.; Mongin, O.; Le Droumaguet, C.; Juikov, V.; Terenziani, F.; Badaeva, E.; Tretiak, S.; Blanchard-Desce, M. Simultaneous control of emission localization and two-photon absorption efficiency in dissymmetrical chromophores. *J. Phys. Chem. B* 2010, 114, 3152–3169. [CrossRef]
47. Merkt, F.K.; Höwedes, S.P.; Gers-Panther, C.F.; Gruber, I.; Jeniak, C.; Müller, T.J.J. Three component activation/alkynylation/cyclocondensation (AACC) synthesis of enhanced emission solvatochromic 3-ethynylquinoxalines. *Chem. Eur. J.* 2018, 24, 8114–8125. [CrossRef]
48. Fecková, M.; Le Poul, P.; Robin-le Guen, F.; Roisnel, T.; Pytela, O.; Klikar, M.; Bureš, F.; Achelle, S.; 2,4-Distyril and 2,4,6-tristyrylpyrimidines: Synthesis and photophysical properties. *J. Org. Chem.* 2018, 83, 11712–11726. [CrossRef]
49. Achelle, S.; Robin-le Guen, F. Emission properties of diazines chromophores: Structure properties relationship. *J. Photochem. Photobiol. A Chem.* 2017, 348, 281–286. [CrossRef]
50. Shen, X.Y.; Yuan, W.Z.; Liu, Y.; Zhao, Q.; Liu, P.; Ma, Y.; Williams, I.D.; Qin, A.; Sun, J.Z.; Tang, B.Z. Fumaronitrile-based fluorogen: Red to near-infrared fluorescence, aggregation-induced emission, solvatochromism, and twisted intramolecular charge transfer. *J. Phys. Chem. C* 2012, 116, 10541–10547. [CrossRef]
51. Gupta, S.; Milton, M.D. Novel Y-shaped AIEE-TICT active π-extended quinoxalines-based donor-acceptor molecules displaying acidofluorochromism and temperature dependent emission. *J. Photochem. Photobiol. A Chem.* 2022, 424, 113630. [CrossRef]
52. Luo, J.; Xie, Z.; Lam, J.W.Y.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H.S.; Zhan, X.; Liu, Y.; Zhu, D.; et al. Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole. *Chem. Commun.* 2001, 18, 1740–1741. [CrossRef] [PubMed]
53. Chen, Y.; Lam, J.W.Y.; Kwok, R.T.K.; Liu, B.; Tang, B.Z. Aggregation-induced emission: Fundamental understanding and future developments. *Mater. Horiz.* 2019, 6, 428–433. [CrossRef]
54. Singer, K.D.; Carito, A.F. Measurements of molecular second order optical susceptibilities usin dc induced second harmonic generation. *J. Chem. Phys.* 1981, 75, 3572. [CrossRef]
55. Levine, B.F.; Bethea, C.G. Molecular hyperpolarizabilities determined from conjugated and nonconjugated liquids. *Appl. Phys. Lett.* 1974, 24, 445. [CrossRef]
56. Ledoux, I.; Zyss, J. Influence of the molecular environment in solution measurements of the second order optical susceptibility for ureand derivatives. *Chem. Phys.* 1982, 73, 203–213. [CrossRef]
57. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Petersson, G.A.; Nakatsuji, H.; et al. Gaussian 16, Revision A.03; Gaussian, Inc.: Wallingford, CT, USA, 2016.
58. Bird, C.W. The application of new aromaticity index to six-membered ring heterocycles. *Tetrahedron* 1986, 42, 89–92. [CrossRef]
59. Bird, C.W. A new aromaticity index and its application to five-membered heterocycles. *Tetrahedron* 1985, 41, 1409–1414. [CrossRef]
60. Kvasshnin, Y.A.; Verbitskiy, E.V.; Zhilina, E.F.; Rusinov, G.L.; Chupakhin, O.N.; Charushin, V.N. Synthesis of Heteroannulated Indolopyrazines through Domino N–H Palladium-Catalyzed/Metal-Free Oxidative C–H Bond Activation. *ACS Omega* 2020, 5, 15681–15690. [CrossRef]
61. Taniguchi, M.; Lindsey, J.S. Database of absorption and fluorescence spectrot >300 common compounds for use in photochem CAD. *Photochem. Photobiol.* 2018, 94, 290–327. [CrossRef]
62. Ulrich, G.; Barsella, A.; Boeglin, A.; Niu, S.; Ziesel, R. BODIPY-bridged push-pull chromophores for nonlinear optical applications. *ChemPhysChem* 2014, 15, 2693–2700. [CrossRef] [PubMed]