EurJOC
European Journal of Organic Chemistry

Chemistry Europe
European Chemical Societies Publishing

Accepted Article

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To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.202000870

Link to VoR: https://doi.org/10.1002/ejoc.202000870

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Electron-withdrawing substituted quinazoline push-pull chromophores: Synthesis, electrochemical, photophysical and second order nonlinear optical properties

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Abstract: A series of chromophores bearing 4-cyanoquinazoline, 2-(4-cyanophenyl)quinazoline or 2-(4-trifluorophenyl)quinazoline electron-acceptor (A) and 5-(4-aminophenyl)thiophen-2-yl or 4-aminophenyl electron-donor (D) units has been designed. The influence of the electron-withdrawing substituent on the pyrimidine core as well as the nature of the amino electron donating group has been studied by cyclic voltammetry, UV-Vis and emission spectroscopy. Whereas 2-(4-cyanophenyl)quinazoline and 2-(4-trifluorophenyl)quinazoline derivatives are highly luminescent in chloroform solution, 4-cyanoquinazolines are poorly emissive. Interestingly all compounds are luminescent in the solid state with the emission ranging from blue to red. The second order nonlinear optical properties were studied using electric field induced second harmonic generation (EFISH) method. Quantum-chemical calculations corroborate the aforementioned experimental results.

Introduction

Over the last 25 years, there has been a considerable interest in the design of organic push-pull chromophores having electron-donating group (D) linked to an electron-withdrawing one (A) via a π-conjugated bridge (D-π-A structure).[1] In these compounds, intramolecular charge transfer (ICT) occurs and generation of new low-energy molecular orbital induces unique optical and electrochemical properties.[2] These chromophores have found key applications as fluorescent sensors,[3] in optoelectronic, particularly for photovoltaics,[4] organic field effect transistor (OFETs)[5] and in organic light emitting diodes (OLEDs).[6] The generation of a molecular dipole in push-pull chromophores induces also nonlinear optical (NLO) properties such as second order NLO phenomena and two-photon absorption (TPA). The second order NLO properties have found applications as second harmonic generation, used for example to obtain green laser from an infrared source at 1064 nm,[7] second harmonic microscopy[8] and terahertz generation.[9] NLO response is directly related to the ICT and can be easily tuned by varying the D/A couple,[1,10] the π-conjugated spacer [1,2,11] or by branching the chromophore to adopt quadrupolar or octupolar structure.[12]

The pyrimidinyl (1,3-diazinyl) fragment has been widely used as electron-deficient part in push-pull structures.[13] The luminescence properties of pyrimidine fluorophores are highly sensible to external stimuli and have been used as sensors of polarity,[14] pH,[14b,c] metal cations[15] and nitrogen explosives.[16] Push-pull pyrimidine derivatives are also well-known for their TPA properties.[17] Some of us have studied the second order NLO properties of pyrimidine chromophores: even if the NLO responses of styrylpyrimidine derivatives remain moderate,[18] extension of the π-conjugated spacer,[19] incorporation of a metal centre between the D/A parts,[20] and reinforcement of the electron-withdrawing character of pyrimidinyl fragment by *N*-complexation or *N*-methylation[21] induce a significant increase of the second order hyperpolarizability tensor. Akdas-Kilig and co-workers have also described octopolar structures based on bipyrimidinyl electron withdrawing central part.[22] On the contrary, quinazoline (benzopyrimidine) chromophores have been studied only recently.[13a,b,23] Some of these compounds exhibit strong luminescence properties.[24] The quinazolinyl moiety can be considered as stronger electron-withdrawing part than the corresponding pyrimidinyl group due to the possibility of extra electron delocalization into the fused benzene ring. Stronger ICT in quinazoline chromophores is illustrated by red-

shifted absorption and emission with regards to their pyrimidine analogues.[13b,24c] To the best of our knowledge, quinazoline chromophores have not been studied for their NLO properties so far, and, therefore, we report herein designed of a series of quinazoline push-pull chromophores **1-3** (Figure 1). In these structures, the electron-withdrawing character of the quinazoline ring is reinforced by cyano and trifluoromethyl substituents. Electrochemical, linear and nonlinear optical properties of these compounds were carefully studied experimentally and theoretically using DFT calculations. The influence of the cyanophenyl- and trifluoromethylphenyl- branches was determined by comparison with already known compound **A**.[24c]

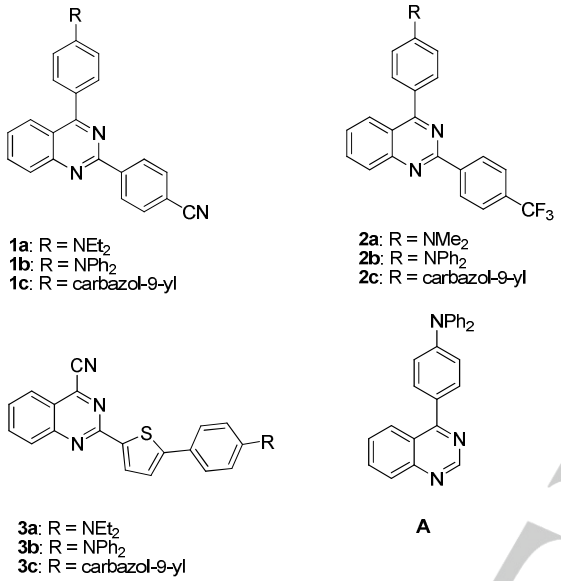
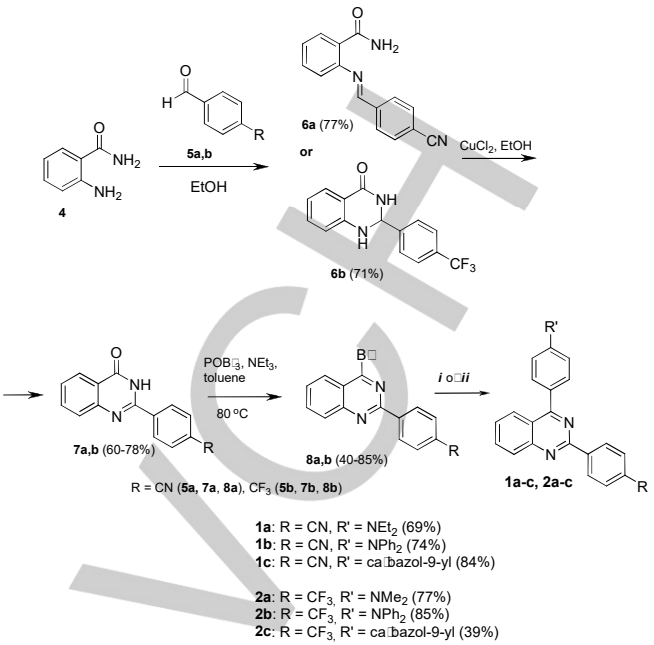


Figure 1. Structures of quinazoline push-pull chromophores **1-3**

Results and Discussion

Synthesis of dyes

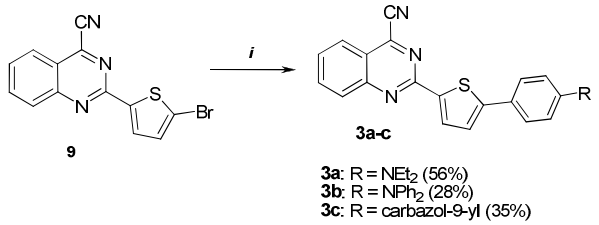
The synthesis of the 2,4-disubstituted quinazolines **1** and **2** is summarized in Scheme 1. Compounds **8a,b** were obtained in three steps following the method similar to reported previously.[25] The condensation of anthranilamide **4** with 4-cyanobenzaldehyde (**5a**) or 4-trifluoromethylbenzaldehyde (**5b**) and subsequent oxidation with copper(II) chloride led to quinazoline-3*H*-ones **7a,b**. It is worth noting that the use of mild conditions (stirring for 5 h at room temperature) gave Schiff base **6a** as condensation product formed by 4-cyanobenzaldehyde **5a**. In the case of 4-trifluoromethylbenzaldehyde **5b** and under the same reaction conditions, the cyclization of Schiff base takes place affording 2,3-dihydroquinazolin-4(1*H*)-one **6b**. This fact corresponds to the published results on interaction between anthranilamides and benzaldehydes under various conditions that reports 2,3-dihydroquinazolin-4(1*H*)-ones as thermodynamic products.[26] ^{1}H NMR spectroscopy of compound **6a** demonstrates signal of N=CH group at δ 8.69 ppm, whereas the spectrum of **6b** contains singlet of aliphatic CH atom at δ 5.86 that is in agreement with the proposed structures (see ESI, Figures S1, S2).



Scheme 1. Synthesis of compounds **1** and **2.** Reagents and conditions: (***i***) Arylboronic acid or arylboronic acid pinacol ester (for **1c**), $PdCl_2(PPh_3)_2$, PPh_3, K_2CO_3, toluene, EtOH, 85 °C, Argon (for **1**); (***ii***) Arylboronic acid, $Pd(PPh_3)_4$, Na_2CO_3, toluene, EtOH, refluxing, N_2 (for **2**).

Both quinazolinones **7a,b** were converted into 4-bromo derivatives **8a,b** by treatment with $POBr_3$ in the presence of Et_3N in toluene. Further, bromo-derivative **8a** subjected to the $PdCl_2(PPh_3)_2$-catalyzed Suzuki-Miyaura cross-coupling reaction with arylboronic acid or 4-(9*H*-carbazol-9-yl)phenylboronic acid pinacol ester to obtain the 4-cyanophenyl quinazolines **1**. Slightly different conditions were applied for the synthesis of CF_3-derivatives **2**, namely, refluxing of bromo-quinazoline **8b** with arylboronic acid in the mixture of toluene and EtOH under N_2, using $Pd(PPh_3)_4$ as a catalyst and saturated solution of Na_2CO_3 as a base.[24c] The quadruplet signals of CF_3 group with J = 272.1–272.9 Hz and carbon atoms (C^3 and C^5) of CF_3-phenyl fragment with J = 3.9 Hz in the ^{13}C NMR of target quinazolines **2** were observed. In the mass spectra of quinazolines **1** the peak of molecular ions with 47% (*m/z* 378 Da for compound **1a**) and with 100% (*m/z* 474 Da and *m/z* 472 Da for compound **1b,c**, respectively) relative intensity were registered.

The synthetic approach to 2-[5-(4-diethylaminophenyl)thiophen-2-yl]quinazoline derivative **3a** has been earlier developed in 56% yield.[27] It includes the condensation of anthranilamide with (thiophen-2-yl)carbaldehyde, chlorodesoxygenation, incorporation of cyano-group at position 4 of quinazoline core, bromination with NBS and subsequent palladium-catalyzed Suzuki-Miyaura cross-coupling reaction**.** The new target chromophores **3b,c** (Scheme 2) have been obtained using the same method. Purification by column chromatography afforded 4-cyanoquinazoline **3b** and **3c** in moderate yields. The structures of the compounds **3b,c** were confirmed by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. The peaks of the corresponding molecular ion (*m/z* 480 and 478 Da, respectively) with 100% relative intensity were observed in their mass spectra.



Scheme 2. Synthesis of 2-(5-(4-aminophenyl)thiophen-2-yl)-4-cyanoquinazolines **3a-c**. Reagents and conditions: (***i***) Arylboronic acid (for **3a,b**) or arylboronic acid pinacol ester (for **3c**), $PdCl_2(PPh_3)_2$, PPh_3, K_2CO_3, toluene, EtOH, 85 °C, argon.

Electrochemical properties

Electrochemical behavior of compounds **1-3** were studied by cyclic voltammetry 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 reference electrode. Ferrocene was used as internal reference for electrochemical measurements. The first oxidation/reduction peak potentials and their differences are listed in Table 1; representative CV diagrams of compounds **1** and **3a** are shown in Figure 2.

Table 1. Electrochemical data of compounds **1**-**3**.

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]
1a	0.553	–2.119	2.67	–5.33	–2.66	464
1b	0.629	–2.053	2.68	–5.41	–2.73	462
1c	0.922[e]	–2.024	2.95	–5.71	–2.76	419
2a	0.584	–2.372[e]	2.96	–5.36	–2.40	419
2b	0.624	–2.129	2.75	–5.40	–2.65	450
2c	0.606[e]	–2.054	2.99	–5.72	–2.73	414
3a	0.312	–1.581	1.89	–5.09	–3.20	655
3b	0.483	–1.570	2.05	–5.26	–3.21	604
3c	0.553[e]	–1.863[e]	2.78	–5.70	–2.92	445

[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 **1**-**3** exhibit an oxidation process with the potential ranging from 0.312 to 0.922 V *vs* ferrocene and a reduction process from -1.570 to -2.372 V (Table 1), influenced by the particular nature of the substituents. When the donor moiety is $NAlk_2$ (**1a**, **2a** and **3a**), the oxidation process is always reversible. The oxidation is irreversible for compounds **1c**, **2c** and **3c** bearing the carbazolyl donor. For these compounds, oxidation leads to the formation of a new electroactive species and an irreversible reduction peak, at lower potential (Ep ≈ -0.5 V) is observed on the reverse scan after the first oxidation. For diphenylamino derivatives **1b** and **2b**, the formation of a deposit on the working electrode is occurred after the first oxidation step and a fine intense signal is observed attributed to the formation dimerization or polymerization products as described in the literature for carbazole and triphenylamine derivatives.[28] Finally, except the chromophore **2a** that exhibits an irreversible reduction signal, a reduction process of compounds **1**-**3** is reversible.

The HOMO/LUMO and electrochemical gap energies for all compounds were calculated from the potentials values. When employing the carbazol-9-yl donor (**1c**, **2c** and **3c**), the oxidation is more difficult than in case of dialkylamino and diphenylamino analogs, while the reduction changes to a lesser extent. In each series, the highest electrochemical band gap is therefore observed for carbazolyl derivatives. The dialkylamino derivatives **1a**, **2a** and **3a** are easier to oxidize but more difficult to reduce than their diphenylamino analogues **1b**, **2b** and **3b**: the gap values are therefore similar for both substituents in each series.

For a given donor substituent, when changing the acceptor from CN to CF_3 group, there is a small shift of the E_{red} values to lower potential values (**1** compared to **2**), indicating a better acceptor ability of the CN group. This electron-withdrawing effect for both compounds **1b** and **2b** is confirmed by the measurement of the reduction potential for their unsubstituted analogue **A** (E_{red}= –3.34 V).

Finally, when the cyano group is on position 4 of the quinazoline ring (compounds **3**), the E_{red} values are less negative than for compounds **1** and **2** pointing to a more electron-withdrawing ability of this moiety. Compounds **3** are also more easily reduced. This trend supports a stronger ICT for these molecules compared to **1** and **2**.

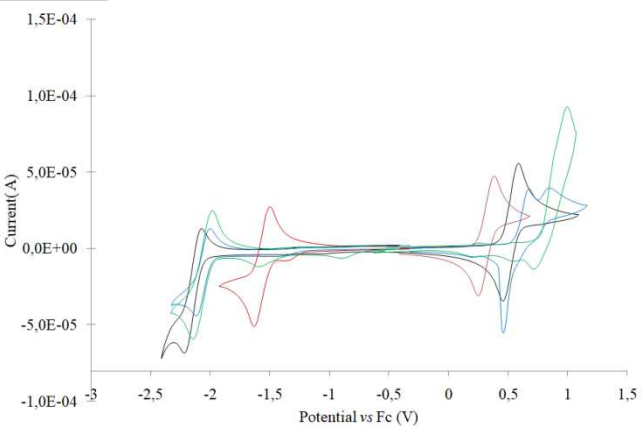


Figure 2. Cyclic voltammograms of chromophores **1a** (black), **1b** (blue), **1c** (green) and **3a** (red) in CH_2Cl_2 solutions with NBu_4PF_6 (0.1M) as the electrolyte: first oxidation and reduction waves.

Linear optical properties

The UV/Vis and photoluminesce (PL) spectroscopic data for compounds **1**-**3** measured in $CHCl_3$ at room temperature are presented in Table 2. The analyses were carried out using low-concentrated solutions of chromophores (0.9-1.7 × 10^{-5} M). As representative examples, normalized spectra of compounds **1** are displayed in Figure 3. Compounds **1** and **2** exhibit charge transfer (CT) absorption band in the UV or purple region with relatively low molar extinction coefficients around 20 mM^{-1} cm^{-1} or below. In each series, the most blue-shifted energetic CT absorption bands are observed for the carbazoyl derivatives, whereas the absorption maxima are similar for dialkylamino and

diphenylamino chromophores. This is in agreement with the electrochemical band gap values. Compounds **1** and **2** exhibit intense blue-green emission with quantum yield > 0.5. Both compounds **1b** and **2b** possess red-shifted emission with regards to their unsubstituted analogue **A**,[24c] indicating a stronger ICT induced by cyanophenyl and trifluoromethylphenyl substituents. Bathochromic shifts of the absorption and emission maxima are observed for cyano derivatives **1** as compared their trifluoromethyl analogues **2**, which is in accordance with the electrochemical behaviour. Diphenylamino derivatives **1b** and **2b** in each series exhibit the most red-shifted emission, as observed in other families of similar push-pull compounds.[14b,19] Compounds **3** are poorly emissive in solution, probably due to twisted intramolecular charge transfer (TICT) excited state. Only carbazole derivative **3c** exhibits a moderate photoluminescence quantum yield of 0.10.

Table 2. UV-Vis and photoluminescence (PL) data of compounds **1**-**3** in $CHCl_3$ solution.

Comp.	λ_{abs}, nm	ε, mM^{-1} cm^{-1}	λ_{em}, nm	Φ_F	Stokes shift, cm^{-1}
1a	408	20.4	496	0.63	4350
1b	402	20.2	531	0.72	6040
1c	363sh 340	8.5 11.4	486	0.64	6970
2a	390	14.5	474	0.76	4540
2b	396	20.9	517	0.75	5910
2c	340	12.3	474	0.53	8310
3a	467sh 403	14.1 28.5	508	> 0.01	1730
3b	441sh 398	17.4 28.8	494	> 0.01	2430
3c	365	29.6	469	0.10	6080

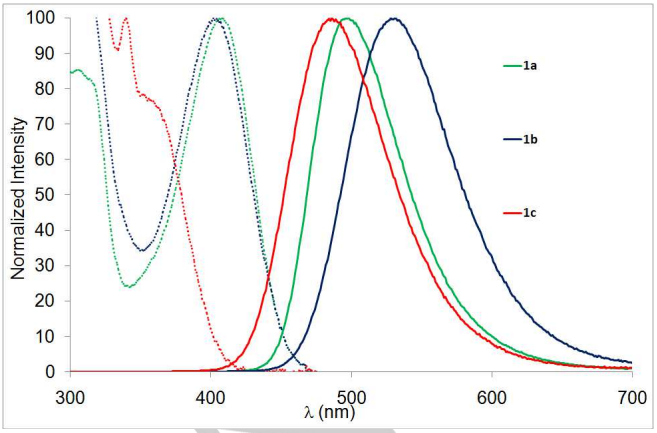


Figure 3. Normalized absorption (dashed line) and emission spectra (solid lines of compounds **1a** (green), **1b** (blue) and **1c** (red) in $CHCl_3$ solution.

Positive fluorosolvatochromism associated with a moderate absorption solvatochromism is characteristic of push-pull fluorophores: a bathochromic shift of the emission band is observed when the polarity is increased, which is due to the stabilization of highly polar excited state in polar solvent.[29] Table 3 displays the emission maxima of compounds **1**-**3** in a series of aprotic solvents of different polarity, evaluated according to the Reichardt polarity scale ($E_T(30)$).[30] Compounds **1**-**3** do not exhibit significant absorption solvatochromism (less than 10 nm difference whatever the solvent) was observed without correlation with solvent polarity. Compounds **1** and **2** exhibit the typical behavior of D-π-A derivatives: for each compound, the emission maxima is proportional to $E_T(30)$ of the corresponding solvent (Figure S29). Figures 4 and 5 (part A) display the normalized spectra and color change in various aprotic solvents upon UV-irradiation of compound **1b**. This compound possesses luminescence from blue in *n*-heptane to orange in MeCN. The slope (m) of the regression line of emission maxima vs $E_T(30)$ is a way to roughly evaluate the ICT.[14c] Compound **1a** exhibits the highest m parameter and compounds **1** show higher m value than the corresponding compounds **2** indicating higher ICT into cyano derivatives **1** than into trifluoromethyl analogues. For compounds **3**, the fluorosolvatochromism behavior is different as shown on Figure 4 (part B): in solvents with lower polarity (*n*-heptane, toluene for all compounds as well as 1,4-dioxane and THF in case of **3c**) the formation of J-aggregate leading to an emission band in the 550-700 nm range is observed.[31] In higher polarity solvents, compounds **3** exhibit classical positive fluorosolvatochromism. The m parameters were calculated using only the data gained from these solvents. Finally, all compounds are emissive in solid state with emission going from blue for **1c** and **2c** to red for **3a** and **3b** (Figure 6).

Table 3. Fluorosolvatochromism of compounds **1**-**3** and **A** in various aprotic solvents and in the solid state.

Comp.	*n*-heptane 30.9 [a]	Toluene 33.9[a]	1,4-dioxane 36.0 [a]	THF 37.4 [a]	DCM 40.7 [a]	MeCN 45.6 [a]	m[b]	Solid state [c]
1a	430	468	483	536	524	604	11.06	502
1b	457	488	502	540	554	604	9.94	505
1c	424	446	460	494	505	558	9.08	451
2a	426	461	477	512	498	563	8.36	469
2b	454	482	495	532	544	589	9.12	526
2c	419	441	454	489	500	553	9.02	454
3a	596	485/ 670	501	511	528	564	6.93	664
3b	573	485/ 623	490	505	517	532	4.23	611
3c	-[e]	452/ 538	456/ 562	453/ 609	478	494	3.71	541
A[23c]	445 [d]	-[e]	-[e]	508	528	559	7.74	-[e]

[a] $E_T(30)$, Reichardt polarity parameter in kcal mol^{-1}.
[b] Slope of the regression line λ_{max} (nm) vs. $E_T(30)$ in nm $kcal^{-1}$.
[c] Powder. [d] in cyclohexane ($E_T(30)$ = 30.9). [e] not measured.

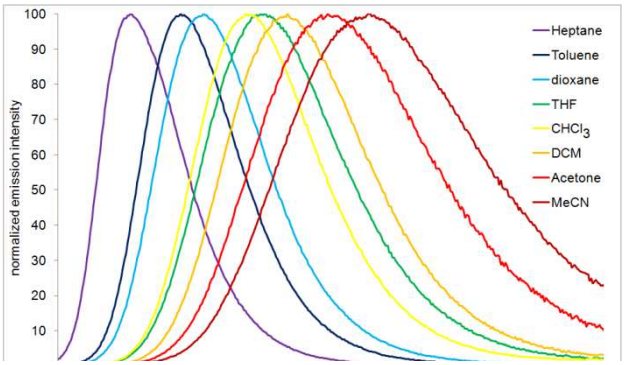


Figure 4. Normalized emission spectra of **1b** in different aprotic solvents.

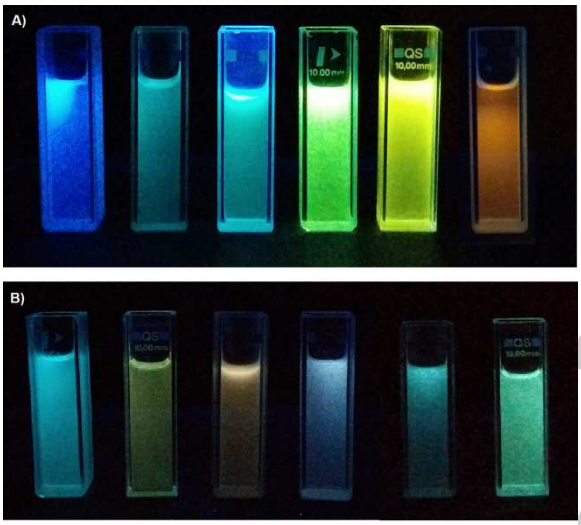


Figure 5. Fluorescence color changes for **1b** (part A) and **3c** (part B) in various solvents (from left to right: *n*-heptane, toluene, 1,4-dioxane, $CHCl_3$, CH_2Cl_2 and MeCN). Photographs were taken in the dark upon irradiation with a hand-held UV lamp (λ_{em} = 366 nm)

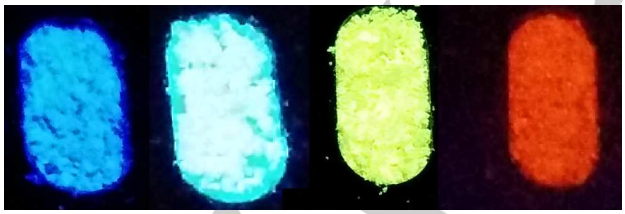


Figure 6. Emission of compounds **1c, 2a, 2b** and **3b** (from left to right) in solid state (powder). Photographs were taken in the dark upon irradiation with a hand-held UV lamp (λ_{em} = 366 nm)

Second order NLO 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 $\beta_{//}$.[32] The results are presented in Table 4. 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 fluorosolvatochromic observation. The NLO responses of compounds **1**-**3** remain moderate mainly due to nonoptimized π-conjugated linkers with the higher $\mu\beta$ values for compounds **3**. In each series, the dialkylamino derivatives exhibit the highest $\mu\beta$ value, followed by diphenylamino derivatives (**2a** and **2b** exhibit even similar values) and the NLO response of carbazole derivatives is significantly lower, at the detection limit of the used technique. A comparison of chromophores **1b** and **2b** with unsubstituted analogue **A** implies that 4-cyanophenyl and 4-trifluoromethylphenyl electron-withdrawing substituents in C2 position of the quinazoline core significantly enhance the NLO response. Moreover, the cyano substituted compounds **1** exhibit significantly higher NLO response than trifluoromethyl substituted chromophores **2** in accordance with higher Hammett constant for cyano group. All these results are in full accordance with the electrochemical and UV-Visible data: NLO responses increase when absorbance maxima are redshifted and electrochemical gap decreased.

Table 4. $\mu\beta$ values for compounds **1**-**3** and **A**.

Comp.	$\mu\beta$, 10^{-48} esu [a]	Comp.	$\mu\beta$, 10^{-48} esu [a]
1a	240	**2c**	<40
1b	140	**3a**	280
1c	<40	**3b**	150
2a	110	**3c**	<40
2b	110	**A**	<40

[a] $\mu\beta$ *(2ω)* at 1907 nm in $CHCl_3$. Molecular concentrations used for the measurements were in the range of 10^{-3} to 10^{-2} M, $\mu\beta \pm 10\%$

Computational studies

Spatial and electronic properties of all target chromophores **1**–**3** were investigated at the DFT level by using the Gaussian® 16 software package.[33] The geometries of molecules were optimized using the DFT B3LYP/6-311+G(2df,p) method. Energies of the HOMO and the LUMO, their differences, ground-state dipole moments μ and first hyperpolarizabilities β (1907 nm) were calculated on the DFT B3LYP/6-311+G(2df,p) level including $CHCl_3$ as a solvent (Table 5).

The calculated HOMO and LUMO energies are within the range of –5.86 to –5.19 and –3.04 to –2.24 eV, respectively. The computed values are in a good agreement with the electrochemically obtained HOMO and LUMO levels as demonstrated by their correlations (Figures S33-S35 in the ESI). Hence, the used DFT method can be considered as appropriate. In all particular series, the HOMO/LUMO decreases within the order of **a**→**b**→**c**; the differences between chromophores **a** and **b** ($NAlk_2$ vs. NPh_2 donors) are relatively small. Carbazolyl-substituted chromophores showed the largest HOMO–LUMO

gaps. Figure 7 shows localization of the HOMO(–1/2) and LUMO(+1/2) as well as Mulliken charges in representative chromophores **1a** and **3a** that differ in the arrangement of the D/A couple and the π-linker extension. As expected, the HOMO(–1/2) in **1a** are mostly spread over the *N,N*-diethylanilino donor, while the LUMO(+1/2) occupy the quinazoline, 4-cyanophenylene as well as phenylene moieties. The HOMO(–1/2) in **3a** is represented by whole 5-(*N,N*-diethylanilino)thiophen-2-yl moiety, the LUMO(+1/2) are centrally spread over the quinazoline and thiophene rings.

Table 5. DFT calculated data of compounds **1**-**3**

Comp.	E_{HOMO} DFT [eV]	E_{LUMO} DFT [eV]	ΔE DFT [eV]	μ [D]	λ_{max} TD-DFT [nm]	β(-2ω,ω,ω) DFT [10^{-30} esu]	E HOMO DFT [eV]
1a	–5.52	–2.44	3.08	12.89	462	104	–5.52
1b	–5.53	–2.54	2.99	10.78	476	139	–5.53
1c	–5.86	–2.64	3.22	9.04	435	51	–5.86
2a	–5.50	–2.27	3.22	10.63	441	93	–5.50
2b	–5.51	–2.24	3.11	8.34	459	125	–5.51
2c	–5.85	–2.51	3.34	6.54	422	43	–5.85
3a	–5.19	–2.89	2.30	8.92	638	587	–5.19
3b	–5.33	–2.97	2.36	5.63	609	551	–5.33
3c	–5.75	–3.04	2.71	3.84	517	182	–5.75

All data calculated at the DFT level by using the Gaussian® 16 software package and DFT B3LYP/6-311+G(2df,p) method in $CHCl_3$. The first hyperpolarizabilities β(-2ω,ω,ω) 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_{states} = 8) B3LYP/6-311+G(2df,p).

The calculated ground state dipole moments range from 3.84 to 12.89 D and reflect the spatial arrangement of the particular chromophores. In general, the carbazolyl-substituted chromophores in series **c** showed the lowest dipole moments, whereas the *N,N*-dialkylamino derivatives in series **a** possess the largest μ values.

Electronic absorption spectra were calculated using TD-DFT method and $CHCl_3$ as a solvent. All spectra are listed in the ESI (Figures S37-S39), the positions of the longest-wavelength absorption maxima are given in Table 5. In general, the calculated spectra are red-shifted compared to the experimental; however, the calculated and experimental λ_{max} values correlate reasonably (Figure S36). For chromophores **1a**-**c** and **2a**-**c**, the longest-wavelength band appearing between 400 and 500 nm is generated by pure HOMO→LUMO transition. Chromophores **3a**-**c** with inversed D-π-A arrangement showed significantly red-shifted longest-wavelength band, which may appear as a shoulder (see the full-range experimental absorption spectra in the ESI Figure S29). Whereas this red-shifted band corresponds to the HOMO→LUMO transition, the band localized between 400 and 500 nm is generated by the HOMO→LUMO+1 transition.

The quadratic hyperpolarizability tensors β have been also calculated. A correlation of the experimental and calculated $\mu\beta$ products (Figure S40) confirms the same trends of both quantities. In general, the calculated β values for diphenylamino derivatives **1b** and **2b** are higher than their respective dialkylamino analogues **1a** and **2a**. The highest NLO responses have been calculated for chromophores **3a** and **3b** similarly as proved by the aforementioned EFISH method.

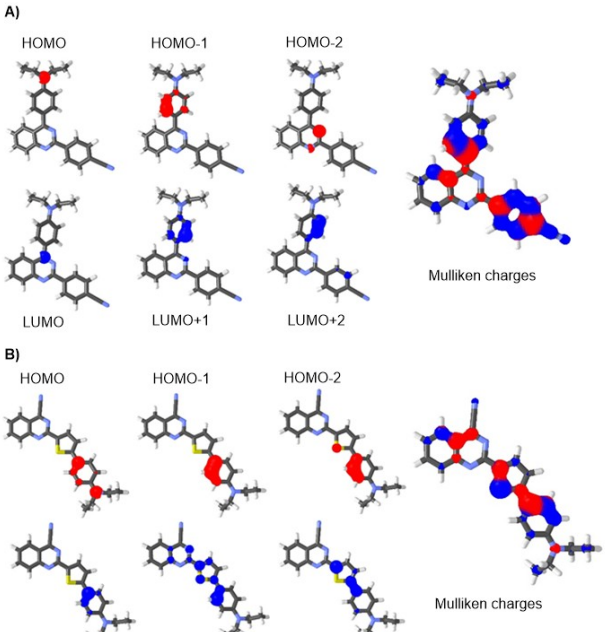


Figure 7. Localization of frontier molecular orbitals and Mulliken charges in representative chromophores **1a** (A) and **3a** (B).

Conclusion

In summary, we have designed and synthesized a series of amino substituted quinazoline push-pull chromophores in which the electron-withdrawing character of the quinazoline core is enhanced by electron-deficient groups, their photophysical and electrochemical properties have been measured. The proposed combination of D and A provided a series of chromophores with wide spectral emission range in both solution and solid state. Compounds with 4-cyanophenyl and 4-trifluoromethylphenyl substituent in C2 position of the quinazoline core exhibited enhanced intramolecular charge transfer with regard to their unsubstituted analogue as shown by their red-shifted absorption and emission spectra as well as their decreased electrochemical gap. These compounds are highly luminescent in chloroform and in the solid state. On the other hand, 4-cyanoquinazolines are poorly emissive in solution but possess red luminescence in the solid state. These compounds exhibit moderate second order NLO response measured by EFISH method. Nevertheless, electron-withdrawing substituents on the quinazoline core induce a significant enhancement of the $\mu\beta$ value. Optimized π-conjugated linkers with phenylenevinylene or thienylenevinylene bridges would probably increase the NLO responses.

Experimental Section

General Information

Unless otherwise indicated, all common reagents and solvents were used from commercial suppliers without further purification. Melting points were measured on the instrument Boetius. TLC was and column chromatography was carried out on SiO_2. ^1H NMR and ^{13}C NMR spectra were recorded at room temperature at 300 and 75.3 MHz respectively, on a Bruker AC-300 spectrometer; at 400 and 100 MHz respectively, on

a Bruker DRX-400 spectrometer; or at 600 MHz on a Bruker DRX-600 spectrometer (^{1}H NMR spectrum for compound **1c**). For compounds **1**, **3b**,**c** and **8a** mass spectra were recorded on the SHIMADZU GCMS-QP2010 Ultra instrument with electron ionization (EI) of the sample. For compounds **2** and **8b**, HRMS spectra were performed at the Centre Régional de Mesures Physiques de l'Ouest" (CRMPO, Université de Rennes1, Rennes, France) using a Bruker MetroTOF-Q II apparatus. Microanalyses (C, H, N) were performed using the Perkin–Elmer 2400 elemental analyzer. The absorption and emission spectra were recorded on Fluoromax-3 spectrophotometer (Jobin-Yvon Horiba). Compounds were excited at their absorption maxima (band or lower energy) to record the emission spectra. All solutions were measured with optical densities below 0.1. Fluorescence quantum yields (± 10%) were determined relative to 9,10-bisphenylethynylanthracene in cyclohexane (Φ_F = 1.00). Stocks shifts were calculated considering the lowest energetic absorption band.

The electrochemical studies of the compounds were performed in a with a 3-electrodes cell (WE: Pt, RE: Ag wire, CE: Pt). Ferrocene was added at the end of each experiment to determine redox potential values. The potential of the cell was controlled by a μAUTOLAB Type III potentiostat monitored by a computer. Anhydrous and freshly distilled dichloromethane was used as solvent and degassed with nitrogen. The supporting salt used was NBu_4PF_6 for electrochemical analysis (>99.9 % Sigma-Aldrich).

Experimental details on EFISH measurements are described elsewhere.[34]

Preparation of intermediates

2-Arylquinazoline-4(*3H*)-ones **(7a,b)** were synthesized in two steps with isolation of intermediate (Schiff base **6a** or dihydroquinazolinone **6b**). Starting compound 2-(5-bromothiophen-2-yl)-4-cyanoquinazoline **9** was synthesized as described in our previous work.[27]

2-(4-Cyanobenzylideneamino)benzamide (**6a**). To a solution of 2-aminobenzamide **4** (0.50 g, 3.7 mmol) in ethanol (9 mL) 4-cyanobenzaldehyde (0.54 g 3.7 mmol) was added. After stirring for 30 minute the precipitate started to drop out. The reaction mixture was summarily stirred during 5 h, and the precipitate was filtered off and washed with EtOH. Yellow solid, yield 77%, mp 189–191 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.25 (d, 1H, *J* = 7.8 Hz, CH benzamide), 7.32 (t, 1H, *J* = 7.4 Hz, CH benzamide), 7.55 (m, 2H, NH, CH benzamide), 7.84 (d, 1H, *J* = 7.8 Hz, CH benzamide), 7.97 (br. s, 1H, NH), 8.03 (d, 2H, *J* = 8.1 Hz, C_6H_4CN), 8.13 (d, 2H, *J* = 8.1 Hz, C_6H_4CN), 8.69 (s, 1H, N=CH). Calcd for $C_{15}H_{11}N_3O$ (249): C 72.28; H 4.45; N 16.86. Found: C 72.21; H 4.32; N 16.84.

2-(4-Trifluoromethylphenyl)-2,3-dihydroquinazolin-4(1*H*)-one (6b). Was synthesized by the same approach as **6a.** Colorless solid, yield 71%, mp 256–258°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.86 (s, 1H, CH), 6.69 (dd, 1H, *J* = 8.1 Hz, *J* = 7.3 Hz, CH), 6.76 (d, 1H, *J* = 8.1 Hz), 7.26 (m, 2H, CH, NH), 7.61 (dd, 1H, *J* = 7.3 Hz, *J* = 1.4 Hz, CH), 7.70 (d, 2H, *J* = 8.4 Hz, $C_6H_4CF_3$), 7.77 (d, 2H, *J* = 8.4 Hz, $C_6H_4CF_3$), 8.44 (s, 1H, NH). Calcd for $C_{15}H_{11}F_3N_2O$ (292): C 61.65; H 3.79; N 9.58. Found: C 61.74; H 3.62; N 9.51.

2-(4-Cyanophenyl)quinazoline-3*H*-one (7a). 2-(4-Cyanobenzylidenamino)benzamide **6a** (0.62 g, 2.5 mmol) was dissolved in ethanol (10 mL), $CuCl_2$ (0.55 g, 4.1 mmol) was added and reaction mixture was refluxed for 2 h. After cooling the formed quinazolinone **6a** was filtered off and recrystallized from DMSO. Colorless solid, yield 60%, mp 276–278 °C (mp lit.[35] 280–282 °C) ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.57 (m, 1H), 7.79–7.87 (m, 2H), 8.05 (m, 2H), 8.17 (br. s, 1H), 8.34 (m, 2H), 12.74 (s, 1H, NH). Calcd for $C_{15}H_9N_3O$ (247): C 72.87; H 3.67; N 16.99. Found: C 72.68; H 3.54; N 16.89.

2-(4-Trifluoromethylphenyl)quinazoline-3*H*-one (7b). Was synthesized by the same approach as **7a.** After cooling of reaction mixture the formed quinazolinone **6b** was filtered off and washed with EtOH. Colorless solid, yield 78%, mp 285–287 °C (mp lit.[34] 280–282 °C) ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.57 (t, 1H, *J* = 7.6 Hz, CH quinaz), 7.77 (d, 1H, *J* = 8.1 Hz, CH quinaz), 7.87 (t, 1H, *J* = 7.6 Hz, CH quinaz), 7.93 (d, 2H, *J* = 8.2 Hz, $C_6H_4CF_3$) 8.17 (d, 1H, *J* = 8.1 Hz), 8.37 (d, 2H, *J* = 8.2 Hz, $C_6H_4CF_3$). Calcd for $C_{15}H_9F_3N_2O$ (290): C 62.07; H 3.13; N 9.65. Found: C 61.98; H 3.02; N 9.46.

2-(4-Cyanophenyl)-4-bromoquinazoline (8a). Was obtained similar to described method.[25] To a suspension of 2-(4-cyanophenyl)quinazolin-4(3*H*)-one **7a** (0.38 g, 1.54 mmol) in toluene (6.8 ml), triethylamine (0.17 ml) and solution of $POBr_3$ (1.75 g, 6.10 mmol) in toluene (3.4 ml) were added. The reaction mixture was stirred at 80 °C for 24 h. After cooling to room temperature the precipitate was filtered off, washed with $NaHCO_3$ solution and dried under reduced pressure. Colorless solid, yield 0.58 g (85%), mp 250–252 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.91 (m, 1H), 8.01 (d, 2H, *J* = 8.2 Hz, C_6H_4CN), 8.13 (m, 2H,), 8.24 (d, 1H, *J* = 8.3 Hz, CH quinaz), 8.66 (d, 2H, *J* = 8.2 Hz, C_6H_4CN). MS (m/z, I_{rel} %): 311 $[M+2]^+$ (23), 309 $[M]^+$ (24), 231 (18), 230 $[M-Br]^+$ (100), 102 (54), 76 (16), 75 (28), 16 (16). Calcd for $C_{15}H_8BrN_3$ (310): C 58.09; H 2.60; N 13.55%. Found: C 58.04; H 2.47; N 13.41.

2-(4-Trifluoromethylphenyl)-4-bromoquinazoline (8b). Was synthesized by the same approach as **8a**. After cooling to room temperature the product was extracted with CH_2Cl_2 (50 ml), organic layer was washed with $NaHCO_3$ solution, then concentrated and dried under reduced pressure. 4-Bromoquinazoline **8b** was extracted with hexane, solvent was removed under reduced pressure, and the product was used without additional purification. Colorless solid, yield 40%, mp 105–107 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.88–7.97 (m, 3H), 8.16 (d, 2H, *J* = 3.7 Hz), 8.23 (d, 1H, *J* = 8.4 Hz, CH quinaz), 8.67 (d, 2H, *J* = 8.2 Hz, $C_6H_4CF_3$). HRMS: found $[M+H]^+$ 352,9896; requires $[M+H]^+$ 352,9896. Calcd for $C_{15}H_8{}^{79}BrF_3N_2$ (352): C 51.02; H 2.28; N 7.93. Found: C 50.90; H 2.13; N 7.67%.

General procedures of Suzuki cross-coupling for the synthesis of quinazolines 1-3.

General procedure I. A solution of bromoquinazoline **8a** or **9** (0.8 mmol) in toluene (15 ml) was stirred at room temperature for 5 min, then the corresponding boronic acid or boronic acid pinacol ester (1 mmol), $PdCl_2(PPh_3)_2$ (15 mg), PPh_3 (11 mg), solution of K_2CO_3 (0.9 g) in water (7.5 ml) and EtOH (8 ml) were added. The mixture was stirred at 85 °C for 7 hours in argon atmosphere in round-bottom pressure flask. After cooling, the target product was filtered off or isolated from the toluene solution.

General procedure II. To the mixture of the 2-(4-trifluorophenyl)-4-bromoquinazoline **8b** (0.25 mmol) in degassed saturated solution of Na_2CO_3 (0.5 mL), ethanol (0.5 mL) and toluene (7.5 mL) the appropriate arylboronic acid (0.5 mmol) and $Pd(PPh_3)_4$ (0.025 mmol) were added. The solution was heated under reflux for 24 h under nitrogen atmosphere. The reaction mixture was cooled and mixture EtOAc/water (1/1, 10 mL) was added. The organic layer was separated and the aqueous layer was extracted with additional EtOAc (2 × 10 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure.

2-(4-Cyanophenyl)-4-(4-diethylaminophenyl)quinazoline (1a). Synthesis was accomplished following the general procedure I. The product was purified by column chromatography (SiO_2, gradually from hexane/EtOAc (10/1) to hexane/EtOAc (1/1)). Yellow solid, yield 69%, mp 155–157 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (t, 6H, *J* = 7.0 Hz, 2(-

CH_3)), 3.49 (q, 4H, $2CH_2$, J = 7.0 Hz), 6.85 (d, 2H, $C_6H_4NEt_2$, J = 8.2 Hz), 7.58 (t, 1H, CH quinaz, J = 7.6 Hz,), 7.80 (d, 2H, C_6H_4CN, J = 7.9 Hz), 7.88 (m, 3H), 8.11 (d,1H, CH quinaz, J = 8.3 Hz), 8.32 (d, 1H, CH quinaz, J = 8.3 Hz), 8.83 (d, 2H, C_6H_4CN, J = 7.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 12.76 (2C, $2CH_3$), 44.68 (2C, $2(CH_2)$), 111.27 (2C, CH), 113.47 (C) , 119.27 (C), 121.96 (C), 123.89 (C), 127.35 (CH), 127.69 (CH), 129.18 (2C, CH), 129.23 (CH), 132.33 (4C, CH), 133.49 (CH), 143.03 (C), 149.64 (C), 152.16 (C), 158.23 (C), 168.21 (C). MS (m/z, I_{rel} %): 379 $[M+H]^+$ (14), 378 $[M]^+$ (47), 364 (28), 363 $[M\text{-}CH_3]^+$ (100), 335 (16), 230 (13), 181 (11), 102 (13). Calcd for $C_{25}H_{22}N_4$ (378): C 79.34; H 5.86; N 14.80. Found: C, 79.41; H, 5.69; N, 14.55%;

2-(4-Cyanophenyl)-4-(4-diphenylaminophenyl)quinazoline (1b). Synthesis was accomplished following the general procedure **I**. The product was purified by column chromatography (SiO_2, gradually from hexane/$CHCl_3$ (5/1) to $CHCl_3$).Yellow solid, yield 74%, mp 205–207 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (t, 2H, NPh_2, J = 7.3 Hz), 7.24 (m, 6H), 7.35 (t, 4H, NPh_2, J = 7.3 Hz), 7.62 (t, 1H, CH quinaz, J = 7.6 Hz), 7.81 (d, 4H, J = 7.8 Hz), 7.92 (t, 1H, CH quinaz, J = 7.6 Hz,), 8.15 (d, 1H, CH quinaz, J = 8.3 Hz), 8.28 (d, 1H, CH quinaz, J = 8.3 Hz), 8.82 (d, 2H, C_6H_4CN, J = 7.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 113.70, 119.16, 121.64, 121.99, 124.23, 125.64, 127.36, 127.78, 129.19, 129.42, 129.70, 130.07, 131.61, 132.41, 133.87, 142.67, 147.17, 150.25, 152.11, 158.31, 167.99. MS (m/z, I_{rel}%): 475 $[M+H]^+$ (37), 474 $[M]^+$ (100), 473 (32), 306 $[M\text{-}NPh_2]^+$ (22), 237 (11), 102 (13), 76 (11). Calcd for $C_{33}H_{22}N_4$ (474): C 83.52; H 4.67; N 11.81. Found: C 83.37; H 4.50; N 11.72.

2-(4-Cyanophenyl)-4-(4-(9*H*-carbazol-9-yl)phenylaminophenyl)-quinazoline (**1c**). Synthesis was accomplished following the general procedure **I**. After cooling and partially evaporating of reaction mixture the precipitate was filtered off and washed with hexane. Colorless solid, yield 84%, mp 235–237 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.34 (t, 2H, CH carbazole, J = 7.5 Hz), 7.49 (t, 2H, CH carbazole, J = 7.5 Hz), 7.62 (d, 2H, J = 7.7 Hz), 7.84 (t, 1H, CH quinaz, J = 7.6 Hz), 7.94 (d, 2H, J = 8.2 Hz), 8.05 (d, 2H, J = 8.2 Hz), 7.84 (t, 1H, CH quinaz, J = 7.6 Hz), 8.23 (m, 3H), 8.28 (m, 2H), 8.37 (d, 1H, CH quinaz, J = 8.2 Hz), 8.83 (d, 2H, C_6H_4CN, J = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 109.95, 113.99, 119.10, 120.61, 120.63, 122.05, 123.90, 126.32, 127.05, 127.11, 128.34, 129.27, 129.70, 131.98, 132.53, 134.33, 136.19, 139.96, 140.69, 142.38, 152.18, 158.51, 167.79. MS (m/z, I_{rel}%): 473 $[M+H]^+$ (37), 472 $[M]^+$ (100), 471 (28), 306 [M-carbazole]$^+$ (25), 236 (22), 102 (11), 76 (18). Calcd for $C_{33}H_{20}N_4$ (472): requires C 83.88; H 4.27; N 11.86. Found: C 83.68; H 4.09; N 11.75.

2-(4-Trifluoromethylphenyl)-4-(4-dimethylaminophenyl)quinazoline (2a). Synthesis was accomplished following the general procedure II. The product was purified by column chromatography (SiO_2, petroleum ether/EtOAc, 9/1). Yellow solid, yield 77%, mp 160-162 °C (mp lit.[36] 136–138 °C).^{1}H NMR (300 MHz, $CDCl_3$): δ 1.55 (s, 6H, $2CH_3$), 6.89 (d, 2H, $C_6H_4NMe_2$, J = 8.3 Hz), 7.57 (t, 1H, CH quinaz, J = 7.8 Hz), 7.82 (d, 2H, $C_6H_4CF_3$, J = 8.0 Hz), 7.86-7.93 (3H, m), 8.13 (d, 1H, CH quinaz, J = 8.4 Hz), 8.29 (d, 1H, CH quinaz, J = 8.4 Hz), 8.82 (d, 2H, $C_6H_4CF_3$, J = 8.0 Hz). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): 40.42 (CH_3), 111.94 (CH), 122.05 (C), 124.51 (q, J = 272.9 Hz, CF_3), 125.15 (C), 125.46 (q, J = 3.9 Hz, CH), 127.17 (CH), 127.61 (CH), 129.03 (CH), 129.30 (CH), 131.74 (CF_3), 132.01 (CH), 133.44 (CH), 142.15 (C), 152.09 (C), 152.26 (C), 158.88 (C), 168.28 (C). HRMS: found $[M+H]^+$ 394.1527; requires $[M+H]^+$ 394.1526. Calcd for $C_{23}H_{18}F_3N_3$ (393): C 70.22; H 4.61; N 10.68. Found: C 70.04; H 4.41; N 10.46.

2-(4-Trifluoromethylphenyl)-4-(4-diphenylaminophenyl)quinazoline (2b). Synthesis was accomplished following the general procedure II. The product was purified by column chromatography (SiO_2, petroleum ether/EtOAc, 19/1). Yellow solid, yield 85%, mp 146-148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.13 (t, 2H, NPh_2, J = 7.1 Hz), 7.24 (m, 6H), 7.32–7.37 (m, 4H), 7.60 (t, 1H, CH quinaz, J = 7.6 Hz), 7.77 (d, 2H, $C_6H_4CF_3$, J = 8.2 Hz), 7.81 (d, 2H, $C_6H_4NPh_2$, J = 8.9 Hz), 7.91 (t, 1H, CH quinaz, J = 7.6 Hz), 8.15 (d, 1H, CH quinaz, J = 8.4 Hz), 8.27 (d, 1H, CH quinaz, J = 8.2 Hz), 8.81 (d, 2H, $C_6H_4CF_3$, J = 8.2 Hz). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): 121.76 (CH), 122.00 (C), 124.19 (CH), 124.51 (q, J = 272.1 Hz, CF_3), 125.53 (q, J = 3.9 Hz, CH), 125.64 (CH), 127.34 (CH), 127.50 (CH), 129.04 (CH), 129.44 (CH), 129.70 (CH), 130.35 (C), 131.64 (CH), 131.89 (C), 132.32 (C), 133.75 (CH), 141.89 (C), 147.27 (C), 150.19 (C), 152.22 (C), 158.94 (C), 167.96 (C). HRMS: found $[M+H]^+$ 518.1844; requires $[M+H]^+$ 518.1839. Calcd for $C_{33}H_{22}F_3N_3$ (517): C 76.58; H 4.28; N 8.12. Found: C 76.53; H 4.08; N 8.01.

2-(4-Trifluoromethylphenyl)-4-(4-(9H-carbazol-9-yl)phenyl)quinazoline (2c). Synthesis was accomplished following the general procedure II. The product was purified by column chromatography (SiO_2, petroleum ether/EtOAc, 9/1) and recrystallization from the mixture of CH_2Cl_2/heptane three times. Colorless solid, yield 39%, mp 212-214 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (t, 2H, CH carbazole, J = 7.6 Hz), 7.48 (t, 2H, CH carbazole, J = 7.6 Hz), 7.61 (d, 2H, J = 8.1 Hz), 7.70 (t, 1H, CH quinaz, J = 7.6 Hz), 7.80–7.88 (m, 4H), 7.99 (t, 1H, CH quinaz, J = 7.6 Hz), 8.16–8.26 (m, 5H), 8.32 (d, 1H, CH quinaz, J = 8.2 Hz), 8.87 (d, 2H, $C_6H_4CF_3$, J = 8.1 Hz). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): 110.00 (CH), 120.56 (CH), 120.63 (CH), 122.06 (C), 123.92 (C), 124.20 (q, J = 272.9 Hz, CF_3), 125.65 (q, J = 3.9 Hz, CH), 126.33 (CH), 127.02 (CH), 127.14 (CH), 128.04 (CH), 129.13 (CH), 129.70 (CH), 132.01 (CH), 134.19 (CH), 136.40 (C), 139.90 (C), 140.78 (C), 141.61 (C), 152.27 (C), 159.11 (C), 167.73 (C). HRMS: found $[M+H]^+$ 516,1685; requires $[M+H]^+$ 516,1682. Calcd for $C_{33}H_{20}F_3N_3$ (515): C 76.88; H 3.91; N 8.15. Found: C 76.68; H 3.72; N 8.09.

2-(5-(4-Diphenylaminophenyl)thiophen-2-yl)-4-cyanoquinazoline (3b). Synthesis was accomplished following the general procedure I. The product was purified by column chromatography (SiO_2, hexane/EtOAc, 5/1). Orange solid, yield 28%, mp 220–222 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06–7.18 (m, 7H), 7.27–7.33 (m, 6H), 7.60 (d, 2H, J = 8.1 Hz), 7.70 (t, 1H, CH quinaz, J = 7.5 Hz), 7.98 (t, 1H, CH quinaz, J = 7.5 Hz), 8.07 (d, 1H, CH quinaz. J = 8.3 Hz), 8.12 (d, 1H, H-3' thioph, J = 4.0 Hz), 8.19 (d, 1H, CH quinaz, J = 8.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 114.36, 122.71, 123.18, 123.65, 123.68, 125.04, 125.28, 126.94, 127.61, 128.90, 129.01, 129.56, 132.11, 136.07, 139.82, 143.52, 147.42, 148.41, 150.40, 151.89, 157.98. MS (m/z, I_{rel}%): 482 $[M+2]^+$ (11), 481 $[M+1]^+$ (36), 480 $[M]^+$ (100), 240 (12). Calcd for $C_{31}H_{20}N_4S$ (480): C 77.48; H 4.19; N 11.66. Found: C 77.41; H 3.99; N 11.48.

2-(5-(4-(9*H*-Carbazol-9-yl)phenyl)thiophen-2-yl)-4-cyanoquinazoline (3c). Synthesis was accomplished using the 9*H*-carbazole-9-(4-phenyl)boronic acid pinacol ester as a reagent following the general procedure **I**. The reaction was carried out for 20 hours. After cooling of reaction mixture the precipitate was filtered off and washed with hexane. Yellow solid, yield 35%, mp 255–257 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (t, 2H, CH carbazole, J = 7.4 Hz), 7.42–7.52 (m, 5H), 7.66 (d, 2H, J = 7.8 Hz), 7.75 (t, 1H, CH quinaz, J = 7.6 Hz), 7.96 (d, 2H, J = 8.0 Hz), 8.02 (t, 1H, CH quinaz, J = 7.6 Hz), 8.11–8.17 (m, 3H), 8.22 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 109.94, 114.34, 120.35, 120.53, 122.88, 123.71, 125.15, 125.33, 126.22, 127.52, 127.65, 128.38, 129.11, 132.03, 133.03, 136.30, 140.80, 141.49, 143.61, 149.08, 151.86, 157.79. MS (m/z, I_{rel}%): 480 $[M+2]^+$ (11), 479 $[M+1]^+$ (35), 478 $[M]^+$ (100), 239 (18), 76 (17). Calcd for $C_{31}H_{18}N_4S$ (478): C 77.80; H 3.79; N 11.71. Found: C 77.58; H 3.74; N 11.82.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (grant numbers 18-03-00112, 19-33-90014).

Analytical studies were carried out using equipment of the Centre for Joint Use «Spectroscopy and Analysis of Organic Compounds» at the Postovsky Institute of Organic Synthesis of the Russian Academy of Sciences (Ural Branch).

Keywords: quinazoline • push-pull derivatives • intramolecular charge transfer • nonlinear chromophores • fluorescence

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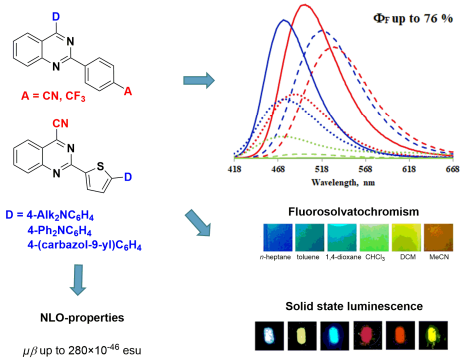

Chromophores: 4-Cyanoquinazoline, 2-(4-cyanophenyl)quinazoline and 2-(4-trifluorophenyl)quinazoline chromophores bearing 5-(4-aminophenyl)thiophen-2-yl or 4-aminophenyl electron-donor (D) units have been synthesized. Data of UV-Vis and emission spectroscopy, cyclic voltammetry, electric field induced second harmonic generation (EFISH) method and quantum-chemical calculations for all compounds have been analyzed.