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Synthesis and Photophysical Studies of a Series of Quinazoline Chromophores

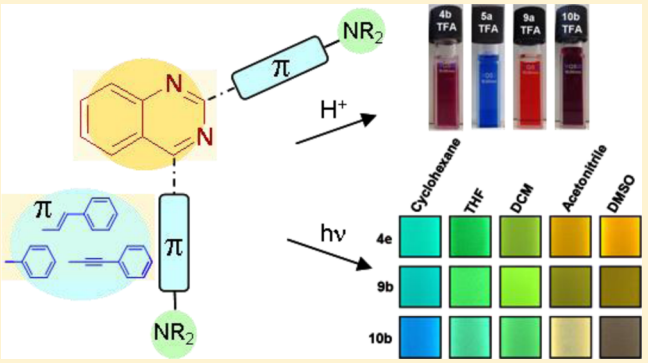
Sylvain Achelle,*[,†] Julián Rodríguez-López,*[,‡] and Françoise Robin-le Guen[†]

[†]Institut des Sciences Chimiques de Rennes UMR CNRS 6226, IUT de Lannion, rue Edouard Branly, BP 30219, F22302 Lannion Cedex, France

[‡]Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, 13071 Ciudad Real, Spain

Supporting Information

ABSTRACT: The synthesis of a series of push−pull arylvinyl (styryl), aryl, and arylethynyl quinazoline derivatives by means of different straightforward protocols is reported. The photophysical properties of the compounds are described. The preparation of arylvinylquinazolines was performed by aldol condensation of the appropriate methylquinazoline and functionalized benzaldehyde. Suzuki and Sonogashira cross-coupling reactions were used to prepare the aryl and arylethynyl compounds, respectively, starting from chloroquinazolines. Optical studies revealed that all of the compounds reported here behave in a way similar to that of their pyrimidine counterparts, with absorption bands in the UV or visible region and the emission of green light upon irradiation. Large red shifts were observed in the fluorescence emission maxima upon increasing the solvent polarity. This strong emission solvatochromism suggests the formation of an intramolecular charge-separated emitting state. The materials can be easily and reversibly protonated at the nitrogen atoms of the heterocyclic ring, and this causes dramatic color changes. This phenomenon opens up the possibility of developing colorimetric pH sensors that can be efficiently modified a posteriori for specific applications.



INTRODUCTION

During the past decade, there has been strong interest in the synthesis of pyrimidine (1,3-diazine) chromophores.[1] The pyrimidine ring is a highly π deficient aromatic heterocycle that can be used as the electron-withdrawing unit in push−pull structures for intramolecular charge transfer (ICT). In general, ICT along the scaffold of the molecule has a significant impact on the luminescence properties and is also required for nonlinear optical (NLO) processes. Moreover, a significant decrease in the HOMO−LUMO energy band gap is observed upon incorporation of pyrimidines in the backbone of π-conjugated structures.[2] Protonation, hydrogen bond formation, and chelation of the nitrogen atoms of the pyrimidine ring are also of great importance. Indeed, such derivatives have been used in the formation of supramolecular assemblies[3] and sensors.[4] In addition, it should be noted that the pyrimidine ring is also an excellent building block for the synthesis of liquid crystals;[5] the combination of the optical and thermal advantages that the pyrimidine provides can lead to completely new applications. Pyrimidine fragments have recently been incorporated into the scaffold of dyes for solar cells, either as π-conjugated linkers between donor and acceptor groups[6] or as electron-accepting TiO_2 anchoring groups.[7]

4,6-Diarylpyrimidines and 2,4,6-triarylpyrimidines, when judiciously substituted with an electron-donating group, are known for their strong emission properties.[8] Similar photophysical behavior was observed with 4,6-bis(arylethynyl)-pyrimidines and 2,4,6-tris(arylethynyl)pyrimidines.[9] In addition to intense fluorescence,[10] electron-donor-substituted 4-(arylvinyl)pyrimidines and 4,6-bis(arylvinyl)pyrimidines are known to exhibit second-[11] and third-order NLO properties.[12] In particular, 4,6-bis(arylvinyl)pyrimidines are now well-established two-photon absorption (TPA) chromophores. Recently, some of us compared the photophysical properties of 2-(arylvinyl)pyrimidines and 4-(arylvinyl)pyrimidines[13] and carried out a statistical study to predict the photophysical properties of pyrimidine derivatives.[14]

In a previous study[11c] we observed a strong enhancement of the fluorescence intensity and the second-order NLO response when comparing quinoxaline (benzopyrazine) and pyrazine derivatives. Taking into account the fact that the pyrimidine ring is better than the pyrazine ring in terms of second-order NLO response, due to its higher electron-donating character,[11c] it seemed of interest to study the photophysical properties of quinazoline (benzopyrimidine) derivatives. Amazingly, this heterocycle has rarely been used in materials chemistry.[15] Only recently have Liu and co-workers described 2,4-diary-

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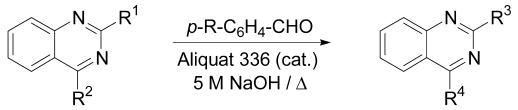
Table 1. Synthesis of Arylvinylquinazolines by Aldol Condensation of Methylquinazolines with Aromatic Aldehydes[c]



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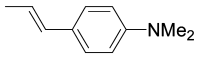
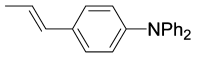
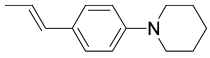
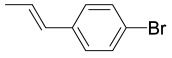
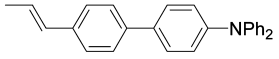
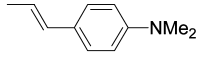
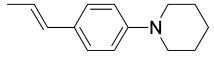
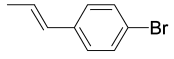
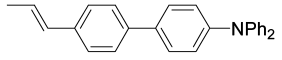
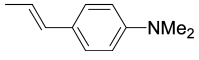
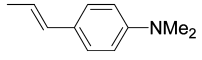
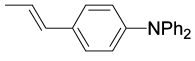
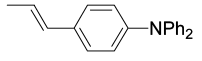
2: R^1 = H, R^2 = Me
3: R^1 = Me, R^2 = Me

4: R^3 = CH=CH-Ar, R^4 = H
5: R^3 = H, R^4 = CH=CH-Ar
6: R^3 = CH=CH-Ar, R^4 = CH=CH-Ar

Reagent	$-R^1$	$-R^2$	Compd	$-R^3$	$-R^4$	Yield (%)[a]
1	Me	H	**4a**		–H	74
1	Me	H	**4b**		–H	71
1	Me	H	**4c**		–H	53
1	Me	H	**4d**		–H	61
1	Me	H	**4e**[b]		–H	85
2	H	Me	**5a**	–H		88
2	H	Me	**5b**	–H		35
2	H	Me	**5c**	–H		53
2	H	Me	**5d**	–H		--
2	H	Me	**5e**	–H		23
3	Me	Me	**6a**			31
3	Me	Me	**6b**			16

[a]Unoptimized isolated yields. [b]Obtained from **4d**. [c]Reagents and conditions: *p*-Ph_2N-C_6H_4-$B(OH)_2$, $Pd(PPh_3)_4$, Na_2CO_3, toluene/H_2O/EtOH, Δ, 15 h.

lquinazoline derivatives that showed white photoluminescence and electroluminescence through controllable acidic protonation.[16]

The aim of the work described here was to synthesize a series of amino-substituted π-conjugated quinazoline derivatives. The photophysical properties, including solvatochromism and pH sensitivity, are reported, and the results are compared with those obtained for their pyrimidine counterparts.

RESULTS AND DISCUSSION

Preparation of Substituted Quinazolines. Different well-established methodologies were used for the preparation of 2-, 4-, and 2,4-(di)substituted quinazolines. Thus, arylvinylquinazoline (styrylquinazoline) derivatives could be easily obtained from the corresponding methylquinazolines by aldol condensation with the appropriate benzaldehyde in boiling aqueous 5 M NaOH using Aliquat 336 as a phase-transfer catalyst, according to the method initially described by Vanden Eynde[17] for methylpyrimidine (Table 1). Conveniently, this synthetic protocol led to the selective formation of *E*-configured vinylene bridges. The yields obtained were usually moderate to good, although in certain cases they were poor due to difficulties in the purification, in particular for 2,4-diarylvinylpyrimidines **6a**,**b**. Biphenyl derivative **4e** was obtained in good yield by a palladium-catalyzed Suzuki cross-coupling reaction[18] from the bromo derivative **4d**. Nevertheless, the analogous 4-substituted compound **5e** was prepared directly by condensation of the corresponding biphenyl aldehyde, taking into account that we were unable to obtain 4-(*p*-bromophenylvinyl)quinazoline (**5d**).

Different aryl- and arylethynylquinazolines could be accessed starting from 4-chloroquinazoline (**7**) and 2,4-dichloroquinazoline (**8**) (Table 2). Whereas 4-arylquinazoline and 2,4-diarylquinazoline derivatives **9** and **10** were obtained by Suzuki cross-coupling reactions using $Pd(PPh_3)_4$ as catalyst, 4-arylethynylquinazoline derivatives **11** and **12** were prepared by copper/palladium-cocatalyzed Sonogashira reactions. It should be noted that the π-electron-deficient character of the quinazoline ring makes the oxidative addition of palladium to a

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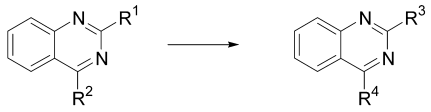
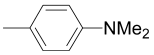
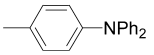
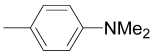
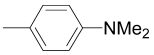
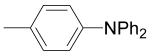
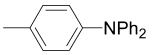
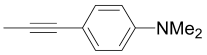
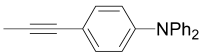
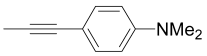
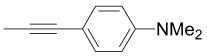
Table 2. Synthesis of Aryl- and Arylethynylquinazolines by Catalyzed Cross-Coupling Reactions from Chloroquinazolines



7: R^1 = H, R^2 = Cl
8: R^1 = Cl, R^2 = Cl

9: R^3 = H, R^4 = Ar
10: R^3 = Ar, R^4 = Ar
11: R^3 = H, R^4 = C≡C−Ar
12: R^3 = Cl, R^4 = C≡C−Ar
13: R^3 = Ph, R^4 = C≡C−Ar

Reagent	Compd	$-R^3$	$-R^4$	Yield (%)[a]
7	**9a**[b]	−H		75
7	**9b**[b]	−H		81
8	**10a**[b]			51
8	**10b**[b]			36
7	**11a**[c]	−H		68
7	**11b**[c]	−H		76
8	**12**[c]	−Cl		70
12	**13**[b]			93

[a]Unoptimized isolated yields. [b]Reagents and conditions: *p*-R-C_6H_4-$B(OH)_2$, $Pd(PPh_3)_4$, Na_2CO_3, toluene/H_2O/EtOH, Δ. [c]Reagents and conditions: *p*-R-C_6H_4-C≡CH, $Pd(PPh_3)_2Cl_2$, CuI, Pr^i_2NH, 70 °C, sealed tube, 15 h.

chloride−carbon bond easier without the use of specialized and expensive ligands.[19] Nevertheless, it was not possible to prepare 2,4-arylethynylquinazolines from **8**. Even when 2.5 equiv of *p*-dimethylphenylacetylene was used, the monosubstituted compound **12** was the only product obtained. A similar difference in reactivity between the 2- and 4-positions of the pyrimidine ring has been reported, with the 2-position known to be less reactive to oxidative addition of palladium than the 4-position.[8,20] Compound **12** was used as the starting material for the synthesis of the differently disubstituted derivative **13**, which was obtained in excellent yield under standard Suzuki conditions.

All of the new materials exhibited good solubility in a variety of solvents, especially in THF and chlorinated solvents. The ^1H and ^{13}C NMR and HRMS data were consistent with the expected structures. As far as the arylvinylquinazolines **4**−**6** are concerned, the ^3J(H,H) coupling constants of ∼16 Hz for the vinylic protons clearly support the selective formation of *E*-configured double bonds. All compounds were perfectly stable in the solid state and could be stored without special precautions. However, it should be noted that some samples underwent partial *trans*−*cis* isomerization when allowed to stand in solution at room temperature for several days.

UV−Vis and Fluorescence Spectroscopy. The photophysical properties of several quinazoline derivatives were examined by UV−vis and fluorescence spectroscopy in dichloromethane (DCM) at 25 °C. The results are given in Table 3 (see also Figure 1 for spectra of compounds **5a**, **9a**, and **11a**).

All compounds showed absorption maxima in the range λ_{max} 370−433 nm (UV or visible region), usually accompanied by a second band at higher energy. With respect to the fluorescence features, typical emission maxima were obtained in the green region. Moreover, the Stokes shifts are rather large, which is a clear indication of the high polarizability of the π-conjugated systems. It is well established that donor−acceptor functionalized molecules can lead to ICT processes, and this would explain the large Stokes shifts.

Both the absorption and emission maxima of 2-arylvinylquinazolines **4** were found to be blue-shifted with respect to those of 4-arylvinylquinazolines **5** with larger fluorescence quantum yields and Stokes shifts. A similar trend was also observed for pyrimidine derivatives.[13,14] Nevertheless, in general, the absorption and emission wavelengths of all the arylvinylquinazolines **4**−**6** are red-shifted in comparison with their previously reported pyrimidine counterparts.[11c,13]

4-Arylquinazolines **9** exhibited the strongest fluorescence response, with quantum yields of up to 0.93. On the other hand, as expected, the absorption and emission of these compounds are blue-shifted in comparison to those of the phenylenevinylene analogues **4**−**5** due to the reduction in the length of the π-conjugated backbone. 2,4-Disubstituted quinazolines **6** and **10** presented absorption and emission bands similar to those of the 4-substituted derivatives **5** and **9**, albeit with higher molar absorption coefficients. The

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Table 3. Optical Spectroscopy Data for Quinazoline Derivatives

compd[a]	λ_{abs}, nm (ε, mM^{-1} cm^{-1})	λ_{em}, nm	Φ_F[b]	Stokes shift, cm^{-1}
4a	255 (17.1), 395 (26.6)	536	0.21	6660
4b	300 (26.0), 400 (33.4)	520	0.61	5769
4c	256 (17.3), 385 (31.8)	545	0.21	7625
4e	308 (30.5), 382 (34.2)	544	0.65	7796
5a	433 (18.0)	548	0.07	4847
5b	302 (21.8), 429 (16.9)	571	0.25	5797
5c	425 (24.9)	558	0.12	5608
5e	309 (28.5), 402 (21.1)	610	0.23	8482
6a	413 (23.1)	545	0.02	5864
6b	299 (31.3), 416 (35.8)	557	0.09	6085
9a	264 (13.8), 380 (16.4)	490	0.93	5908
9b	293 (16.7), 384 (16.6)	528	0.80	7102
10a	341 (36.3), 370 (33.3)	530	0.30	8159
10b	296 (34.7), 384 (37.0)	534	0.34	6474
11a	282 (18.1), 411 (27.5)	560	0.03	6474
11b	295 (20.6), 414 (29.2)	565	0.41	6455
13	269 (43.1), 413 (30.3)	551	0.06	6064

[a]All spectra were recorded in DCM solutions at room temperature at c = (1.0–6.0) × 10^{-5} M for absorption and c = (1.0–6.0) × 10^{-6} M for emission. [b]Fluorescence quantum yield (±10%) determined relative to quinine sulfate in 0.1 M H_2SO_4 (Φ_F = 0.54) and 9,10-diphenylanthracene in cyclohexane (Φ_F = 0.90) as standards.

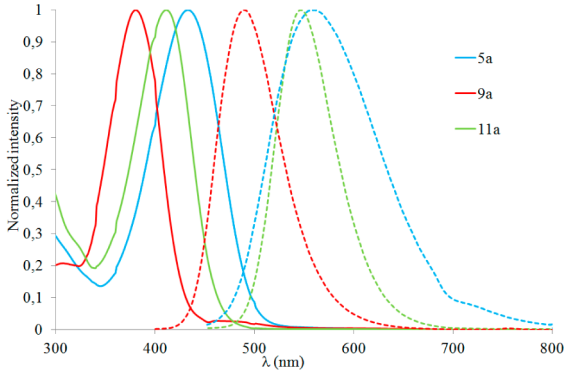

Figure 1. Normalized UV/vis (solid lines) and emission spectra (dashed lines) of compounds **5a**, **9a**, and **11a**.

fluorescence quantum yields, however, were appreciably lower. The most red-shifted emission of the series corresponded to arylethynyl derivatives **11**.

In an effort to gain further insights into the photophysical process within these push–pull molecules, the absorption and emission behavior of the prepared compounds was studied in a variety of different aprotic solvents. While the absorption maxima were not significantly shifted, an increase in solvent polarity led to bathochromic shifts of the emission maxima along with a successive decrease in the fluorescence intensity (Table 4). As an example, the spectra registered for compound **4a** are shown in Figure 2, where the emission wavelength maximum at λ_{em} 443 nm in the least polar solvent (cyclohexane) is red-shifted by about $\Delta\lambda_{em}$ = 151 nm ($\Delta\nu_{em}$ 5738 cm^{-1}) on using DMSO as solvent (λ_{em} 594 nm). The change in the emission color can be easily seen by the naked eye, as shown in Figure 3 for compounds **4e**, **9b**, and **10b**. In general, a strong solvatochromism effect can be observed for the emission features, with a regular trend according to the $E_T(30)$ Dimroth–Reichardt polarity parameters (see the Supporting Information).[21] This solvatochromic behavior, which results from the stabilization of the highly polar emitting state by polar solvents, is typical for compounds that exhibit an internal charge transfer upon excitation and has been fully documented with donor–acceptor fluorophores.[22]

Table 4 shows that 2-arylvinylquinazoline derivatives **4a**,**b** present a larger emission solvatochromism than the 4-substituted compounds **5a**,**b**. As expected, the biphenyl derivatives **4e** and **5e** exhibit a more significant charge transfer than their analogues with only one phenyl ring (**4b** and **5b**). Meanwhile, the 2,4-disubstituted derivative **6a** shows an even smaller fluorosolvatochromism than its 4-substituted analogue **5a**. Comparison of compounds **5a** ($\Delta\lambda_{em}$ = 97 nm, $\Delta\nu_{em}$ = 3398 cm^{-1}), **9a** ($\Delta\lambda_{em}$ = 122 nm, $\Delta\nu_{em}$ = 5337 cm^{-1}), and **11a** ($\Delta\lambda_{em}$ = 139 nm, $\Delta\nu_{em}$ = 5370 cm^{-1}) shows that the aryl (**9a**) and arylethynyl (**11a**) derivatives exhibit stronger internal charge transfer than the arylvinyl derivative (**5a**). However, it is worth noting that, according to the data reported previously by some of us for arylvinylquinoxaline and arylvinylpyrimidine derivatives,[11c,13] a clear trend cannot be observed for each substituent. Moreover, in contrast to the result that one might expect, the fluorosolvatochromism is not always larger for quinazoline derivatives.

It has been demonstrated previously that diazine derivatives can function as colorimetric and luminescent pH sensors due to the basic character of the nitrogen atoms of the heterocycles.[4b,10b,c,11c,13,16,23] The quinazolines described in this paper were not an exception, as evidenced by the significant color change experienced by their DCM solutions upon the addition of TFA (Figure 4), a change that was fully reversible by neutralization with base (Et_3N or KBu^tO).

The changes observed in the UV–vis spectra of **4a** upon addition of acid are illustrated in Figure 5. The increase in the concentration of TFA led to the progressive attenuation of the absorption band for the neutral compound and the appearance of a new, more intense red-shifted band corresponding to the protonated species (see th eSupporting Information for spectra of compounds **5a**, **9a**, and **11a**). This bathochromic shift of the absorption can be explained by an increased charge transfer from the donors to the quinazoline moiety. Similarly to the pyrimidine derivatives,[11c,13] the electron-donating character of the chain at position 2 increases the basicity of the heterocyclic ring, which should be selectively protonated over the aromatic amine. Nonetheless, although the nitrogen at position 3 is initially the most basic center of the quinazoline unit, it is difficult to predict which nitrogen atom is likely protonated (or both). As far as the fluorescence response is concerned, the emission is totally quenched after protonation, as is generally observed for amino electron donor substituted diazines.[11c] Even though these experiments were carried out in an organic solvent (DCM), we recently showed that pyrimidine chromophores can be incorporated into pluronic nanoparticles and used as pH sensors in aqueous media.[24]

CONCLUSIONS

In summary, we have successfully synthesized and characterized a series of push–pull quinazoline derivatives by different, well-established, and straightforward methodologies. Arylvinylquinazolines were prepared by aldol condensation of the appropriate methylquinazoline and aromatic aldehyde, while aryl- and arylethynylquinazolines were accessed by catalyzed cross-coupling reactions from the corresponding chloroquinazoline. All of the molecules displayed optical features that were

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Table 4. Emission Solvatochromism of Quinazoline Derivatives in Various Aprotic Solvents

	λ_{em}, nm					
	cyclohexane, $E_T(30)^a$ = 30.9	THF, $E_T(30)^a$ = 37.4	DCM, $\Delta E_T(30)^a$ = 40.7	acetonitrile, $\Delta E_T(30)^a$ = 45.6	DMSO, $\Delta E_T(30)^a$ = 45.1	$\Delta\nu_{em}$,^{b} cm^{-1}
4a	443	520	536	582	594	5738
4b	449	498	520	543	547	3990
4c	453	522	545	592	600	5408
4e	455	516	544	579	585	4884
5a	465, 488	537	548	572	585	3398
5b	463, 491	540	571	598	600	3700
5c	480, 495	540	558	579	589	3224
5e	461, 490	572	610	642	641	4808
6a	503	540	545	570	580	2639
9a	421	483	490	529	543	5337
9b	445	508	528	559	563	4710
10a	436	528	530	571	575	5544
10b	447	518	534	565	568	4765
11a	444	540	560	573	583	5370
11b	433, 453 (sh)	535	565	610	616	5841
13	423, 442	549	551	570	584	5501

^{a}Dimroth−Reichardt polarity parameter, in kcal mol^{-1}. $^b\Delta\nu_{em} = \nu$(cyclohexane) − ν(DMSO).

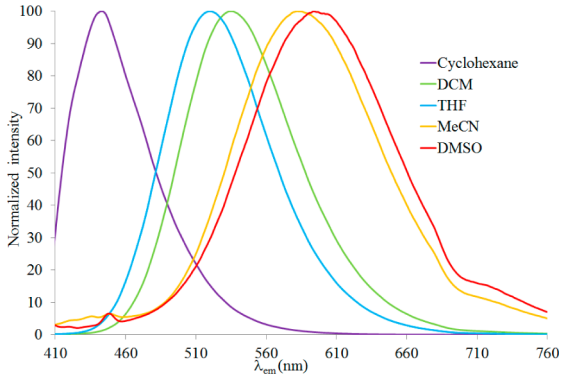

Figure 2. Normalized emission of compound **4a** in different aprotic solvents.

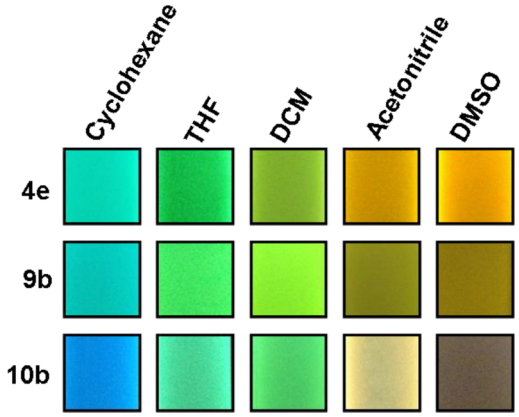

Figure 3. Fluorescence color changes experienced by **4e**, **9b**, and **10b** in various solvents. Squares are trimmed parts of photographs taken in the dark upon irradiation with a hand-held UV lamp (λ_{em} 366 nm).

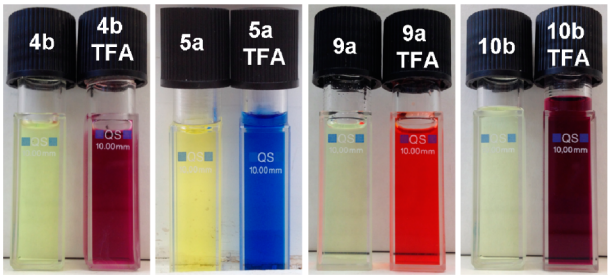

Figure 4. Color change of DCM solutions of several quinazoline derivatives in the presence of TFA.

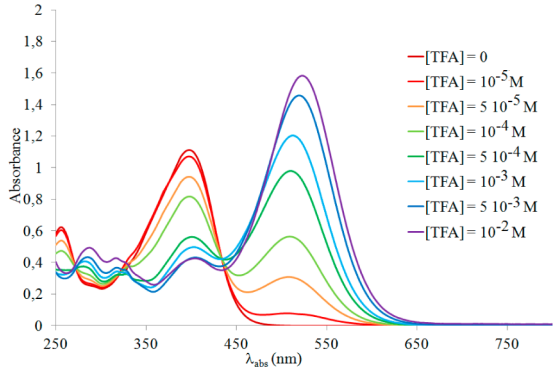

Figure 5. Changes in the absorption of **4a** ($c = 4.1 \times 10^{-5}$ M in DCM) with increasing concentration of TFA.

similar to those of their pyrimidine counterparts. In general, absorption wavelengths were located in the UV or visible region, with typical emission maxima in the green region that led to large Stokes shifts. In particular, the arylquinazoline derivatives exhibited high fluorescence quantum yields. Strong emission solvatochromism was also observed in a variety of nonpolar solvents, a finding that supports the formation of very polar excited ICT states when terminal electron-donating groups are present in the molecule and suggests the potential of the quinazoline structures for NLO studies. Moreover, as one would expect, the materials underwent a dramatic and reversible color change upon addition of acid as a result of the protonation of the nitrogen atoms of the quinazoline ring. This phenomenon should enable the development of colorimetric pH sensors after suitable design of the molecules.

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EXPERIMENTAL SECTION

General Considerations. 4-Chloroquinazoline and 2,4-dichloroquinazoline were purchased from Interchim. 2-Methylquinazoline (**1**) was obtained from 2-bromobenzaldehyde and acetamidine hydrochloride as described previously.[25] 4-Methylquinazoline (**2**) and 2,4-dimethylquinazoline (**3**) were obtained from the corresponding chloro derivatives according to a reported procedure.[26] For air- and moisture-sensitive reactions, all glassware was flame-dried and cooled under nitrogen. NMR spectra were acquired at room temperature. Chemical shifts are given in parts per million relative to TMS (^{1}H, 0.0 ppm) and $CDCl_3$ (^{13}C, 77.0 ppm). Acidic impurities in $CDCl_3$ were removed by treatment with anhydrous K_2CO_3. UV−vis and fluorescence spectra were recorded using standard 1 cm quartz cells. Compounds were excited at their absorption maxima (band of lowest energy) to record the emission spectra. The Φ_F values were calculated using a well-known procedure with two different standards: quinine sulfate in 0.1 M H_2SO_4 and 9,10-diphenylanthracene in cyclohexane.[27] Stokes shifts were calculated by considering the lowest energetic absorption band.

General Procedure for the Synthesis of Arylvinylquinazolines (Styrylquinazolines). A stirred mixture of the corresponding methylquinazoline (0.5 mmol) and the appropriate aldehyde (0.5 mmol, 1 mmol for 2,4-dimethylquinazoline) in aqueous sodium hydroxide (5 M, 10 mL) containing Aliquat 336 (22 mg, 0.05 mmol) was heated under reflux for 2 h. The mixture was cooled. The precipitate was filtered off, washed with water, and purified by column chromatography.

(*E*)-2-(4-Dimethylaminostyryl)quinazoline (4a). Purified by column chromatography (SiO_2, petroleum ether/EtAcO, 1/1). Yellow solid. Yield: 74% (101 mg). Mp: 142−143 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.02 (s, 6H), 6.73 (d, 2H, J = 8.7 Hz), 7.21 (d, 1H, J = 15.6 Hz), 7.59−7.53 (m, 3H), 7.86−7.82 (m, 2H), 7.94 (d, 1H, J = 8.7 Hz), 8.09 (d, 1H, J = 15.9 Hz), 9.32 (s, 1H). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 162.2 (C), 160.1 (CH), 151.1 (C), 150.8 (C), 139.1 (CH), 134.0 (CH), 129.2 (CH), 127.9 (CH), 127.2 (CH), 126.5 (CH), 124.3 (C), 123.12 (C), 123.06 (CH), 112.1 (CH), 40.3 (CH_3). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{18}H_{18}N_3$ $[M + H]^+$ 276.1501, found 276.1501.

(*E*)-2-(4-Diphenylaminostyryl)quinazoline (4b). Purified by column chromatography (SiO_2, petroleum ether/EtAcO, 7/3). Yellow solid. Yield: 71% (141 mg). Mp: 154−155 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.06−7.03 (m, 4H), 7.13−7.10 (m, 4H), 7.29−7.23 (m, 5H), 7.55−7.50 (m, 3H), 7.85−7.81 (m, 2H), 7.94 (d, 1H, J = 8.7 Hz), 8.09 (d, 1H, J = 15.9 Hz), 9.32 (s, 1H). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 161.7 (C), 160.2 (CH), 150.7 (C), 148.8 (C), 147.3 (C), 138.2 (CH), 134.2 (CH), 129.7 (C), 129.4 (CH), 128.7 (CH), 128.0 (CH), 127.2 (CH), 126.9 (CH), 125.7 (CH), 125.1 (CH), 123.6 (CH), 123.2 (C), 122.5 (CH). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{28}H_{22}N_3$ $[M + H]^+$ 400.1813, found 400.1820.

(*E*)-2-(4-Piperidin-1-ylstyryl)quinazoline (4c). Purified by column chromatography (SiO_2, petroleum ether/EtAcO, 7/3). Yellow solid. Yield: 53% (83 mg). Mp: 154−155 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.72−1.66 (m, 6H), 3.31−3.27 (m, 4H), 6.95 (d, 2H, J = 9.0 Hz), 7.25 (d, 1H, J = 15.9 Hz), 7.60−7.54 (m, 3H), 7.90−7.85 (m, 2H), 7.97 (d, 1H, J = 8.7 Hz), 8.11 (d, 1H, J = 15.9 Hz), 9.36 (s, 1H). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 162.0 (C), 160.1 (CH), 152.4 (C), 150.8 (C), 138.8 (CH), 134.1 (CH), 129.0 (CH), 127.9 (CH), 127.2 (CH), 126.6 (CH), 126.2 (C), 124.1 (CH), 123.2 (C), 115.4 (CH), 49.6 (CH_2), 25.6 (CH_2), 24.4 (CH_2). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{21}H_{22}N_3$ $[M + H]^+$ 316.1814, found 316.1819.

(*E*)-2-(4-Bromostyryl)quinazoline (4d). Purified by column chromatography (SiO_2, petroleum ether/EtAcO, 7/3). Colorless solid. Yield: 61% (95 mg). Mp: 179−180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (d, 1H, J = 15.9 Hz), 7.54 (s, 4H), 7.64−7.59 (m, 1H), 7.93−7.88 (m, 2H), 8.01 (d, 1H, J = 9.0 Hz), 8.09 (d, 1H, J = 15.9 Hz), 9.38 (s, 1H). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 161.0 (C), 160.3 (CH), 150.6 (C), 137.2 (CH), 135.2 (C), 134.3 (CH), 132.0 (CH), 129.1 (CH), 128.6 (CH), 128.2 (CH), 127.3 (CH), 127.2 (CH), 123.4 (C), 123.1 (C). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{16}H_{12}N_2{}^{79}Br$ $[M + H]^+$ 311.0184, found 311.0179.

(*E*)-2-[4-(4-Diphenylaminophenyl)styryl]quinazoline (4e). A stirred mixture of **4d** (41 mg, 0.13 mmol), 4-diphenylaminophenylboronic acid (58 mg, 0.20 mmol), and $Pd(PPh_3)_4$ (15 mg, 0.013 mmol) in degassed aqueous 1 M sodium carbonate (0.5 mmol, 0.5 mL)/ethanol (0.5 mL)/toluene (5 mL) was heated under reflux for 15 h under a nitrogen atmosphere. The reaction mixture was cooled and filtered, and EtAcO/water 1/1 (20 mL) was added. The organic layer was separated, and the aqueous layer was extracted with additional EtAcO (2 × 10 mL). The combined organic extracts were dried over $MgSO_4$, and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, petroleum ether/EtAcO, 1/1). Orange solid. Yield: 85% (52 mg). Mp: 221−222 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.08−7.03 (m, 2H), 7.17−7.14 (m, 6H), 7.43−7.29 (m, 4H), 7.45 (d, 1H, J = 15.9 Hz), 7.50 (d, 2H, J = 8.7 Hz) 7.66−7.60 (m, 3H), 7.74 (d, 2H, J = 8.1 Hz), 7.93−7.88 (m, 2H), 8.02 (d, 1H, J = 9.0 Hz), 8.20 (d, 1H, J = 15.9 Hz), 9.40 (s, 1H). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 161.4 (C), 160.2 (CH), 150.7 (C), 147.6 (C), 147.5 (C), 141.2 (C), 138.2 (CH), 134.7 (C), 134.23 (CH), 134.15 (C), 129.3 (CH), 128.2 (CH), 128.1 (CH), 127.6 (2 × CH), 127.2 (CH), 127.1 (CH), 126.9 (CH), 124.6 (CH), 123.7 (C), 123.4 (C), 123.1 (CH). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{34}H_{26}N_3$ $[M + H]^+$ 476.2127, found 476.2130.

(*E*)-4-(4-Dimethylaminostyryl)quinazoline (5a). Purified by column chromatography (SiO_2, petroleum ether/EtAcO, 1/1). Orange solid. Yield: 88% (120 mg). Mp: 139−140 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.03 (s, 6H), 6.72 (d, 2H, J = 8.7 Hz), 7.63−7.59 (m, 3H), 7.68 (d, 1H, J = 15.3 Hz), 7.84 (dt, 1H J_1 = 8.1 Hz, J_2 = 1.2 Hz), 7.98 (d, 1H, J = 8.4 Hz), 8.24 (d, 1H, J = 15.9 Hz), 8.29 (d, 1H, J = 8.4 Hz), 9.20 (s, 1H). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 162.8 (C), 154.8 (CH), 151.5 (C), 150.9 (C), 140.5 (CH), 133.2 (CH), 129.8 (CH), 128.8 (CH), 127.0 (CH), 124.0 (CH), 123.8 (C), 123.0 (C), 114.9 (CH), 112.0 (CH), 40.2 (CH_3). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{18}H_{18}N_3$ $[M + H]^+$ 276.1501, found 276.1500.

(*E*)-4-(4-Diphenylaminostyryl)quinazoline (5b). Purified by column chromatography (SiO_2, petroleum ether/EtAcO, 7/3). Orange solid. Yield: 35% (69 mg). Mp: 118−119 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12−7.06 (m, 4H), 7.17−7.13 (m, 4H), 7.35−7.28 (m, 4H), 7.58 (d, 2H, J = 8.7 Hz), 7.67−7.62 (m, 1H), 7.78 (d, 1H, J = 15.3 Hz), 7.90−7.85 (m, 1H), 8.02 (d, 1H, J = 8.4 Hz), 8.24 (d, 1H, J = 15.3 Hz), 8.29 (d, 1H, J = 8.4 Hz), 9.24 (s, 1H). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 162.4 (C), 154.8 (CH), 151.1 (C), 149.5 (C), 147.0 (C), 139.5 (CH), 133.4 (CH), 129.5 (CH), 129.2 (CH), 129.1 (C), 129.0 (CH), 127.3 (CH), 125.3 (CH), 124.2 (CH), 123.9 (CH), 123.0 (C), 122.0 (CH), 117.8 (CH). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{28}H_{22}N_3$ $[M + H]^+$ 400.1813, found 400.1818.

(*E*)-4-(4-Piperidin-1-ylstyryl)quinazoline (5c). Purified by column chromatography (SiO_2, petroleum ether/EtAcO, 7/3). Yellow solid. Yield: 53% (83 mg). Mp: 96−100 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.70−1.63 (m, 6H), 3.33−3.29 (m, 4H), 6.94 (d, 2H, J = 8.7 Hz), 7.66−7.61 (m, 3H), 7.74 (d, 1H, J = 15.9 Hz), 7.87 (dt, 1H J_1 = 8.1 Hz, J_2 = 1.2 Hz), 8.00 (d, 1H, J = 8.4 Hz), 8.24 (d, 1H, J = 15.9 Hz), 8.31 (d, 1H, J = 8.4 Hz), 9.21 (s, 1H). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 162.7 (C), 154.9 (CH), 152.8 (C), 151.0 (C), 140.1 (CH), 133.3 (CH), 129.7 (CH), 128.9 (CH), 127.1 (CH), 126.4 (C), 124.0 (CH), 123.0 (C), 116.0 (CH), 115.1 (CH), 49.3 (CH_2), 25.5 (CH_2), 24.3 (CH_2). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{21}H_{22}N_3$ $[M + H]^+$ 316.1814, found 316.1815.

(*E*)-4-[4-(4-Diphenylaminophenyl)styryl]quinazoline (5e). Purified by column chromatography (SiO_2, petroleum Ether/EtAcO, 1/1). Yellow solid. Yield: 23% (55 mg). Mp: 151−154 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.08−7.03 (m, 2H), 7.17−7.12 (m, 6H), 7.31−7.24 (m, 4H), 7.53 (d, 2H, J = 8.7 Hz,), 7.70−7.65 (m, 3H), 7.79 (d, 2H, J = 8.7 Hz), 7.93−7.88 (m, 1H), 7.96 (d, 1H, J = 15.9 Hz), 8.06 (d, 1H, J = 8.1 Hz), 8.33 (d, 1H, J = 15.9 Hz), 8.35 (d, 1H, J = 8.1 Hz), 9.30 (s, 1H). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 162.1 (C), 154.8 (CH), 151.1 (C), 147.8 (C), 147.5 (C), 142.0 (C), 139.5

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(CH), 134.3 (C), 133.8 (C), 133.6 (CH), 129.3 (CH), 129.2 (CH), 128.6 (CH), 127.7 (CH), 127.5 (CH), 127.0 (CH), 124.7 (CH), 124.5 (CH), 123.6 (CH), 123.2 (CH), 123.1 (C), 119.9 (CH). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{34}H_{26}N_3$ $[M + H]^+$ 476.2127, found 476.2125.

(*E,E*)-2,4-Bis(4-dimethylaminostyryl)quinazoline (6a). Purified by column chromatography (SiO_2, petroleum ether/EtAcO, 1/1). Orange solid. Yield: 31% (65 mg). Mp: 110−112 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.05 (s, 6H), 3.08 (s, 6H), 6.77 (d, 2H, J = 8.7 Hz), 6.78 (d, 2H, J = 8.7 Hz), 7.25 (d, 1H, J = 15.9 Hz), 7.55 (dt,1H, J_1 = 8.1 Hz, J_2 = 1.2 Hz), 7.65 (d, 2H, J = 8.7 Hz), 7.70 (d, 2H, J = 8.7 Hz), 7.78 (d, 1H, J = 15.9 Hz), 7.81 (dt,1H, J_1 = 8.1 Hz, J_2 = 1.2 Hz), 7.94 (d, 1H, J = 8.4 Hz), 8.20 (d, 1H, J = 15.9 Hz), 8.26 (d, 1H, J = 8.4 Hz), 8.33 (d, 1H, J = 15.9 Hz). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 162.3 (C), 161.3 (C), 151.8 (C), 151.4 (C), 150.9 (C), 139.8 (CH), 138.2 (CH), 133.1 (CH), 129.7 (CH), 129.0 (CH), 128.4 (CH), 125.7 (CH), 124.9 (C), 124.3 (C), 124.2 (CH), 124.0 (CH), 121.3 (C), 115.8 (CH), 112.2 (CH), 112.0 (CH), 40.3 (CH_3), 40.2 (CH_3). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{28}H_{29}N_4$ $[M + H]^+$ 421.2392, found 421.2390.

(*E,E*)-2,4-Bis(4-diphenylaminostyryl)quinazoline (6b). Purified by column chromatography (SiO_2, petroleum ether/EtAcO, 7/3). Yellow solid. Yield: 16% (54 mg). Mp: 124−125 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18−7.06 (m, 16H), 7.34−7.28 (m, 8H), 7.51−7.69 (m, 6H), 7.78 (d, 1H, J = 15.9 Hz), 7.82 (dt,1H, J_1 = 8.1 Hz, J_2 = 1.2 Hz), 7.95 (d, 1H, J = 8.4 Hz), 8.17 (d, 1H, J = 15.9 Hz), 8.23 (d, 1H, J = 8.4 Hz), 8.32 (d, 1H, J = 15.9 Hz). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 162.0 (C), 160.8 (C), 151.8 (C), 149.3 (C), 148.5 (C), 147.4 (C), 147.1 (C), 139.1 (CH), 137.5 (CH), 131.3 (CH), 130.2 (C), 129.7 (CH), 129.5 (CH), 129.4 (CH), 129.1 (CH), 128.6 (CH), 126.3 (CH), 125.2 (CH), 125.1 (CH), 125.0 (CH), 123.8 (CH), 123.4 (CH), 122.7 (CH), 122.2 (CH), 121.5 (C), 119.4 (CH), 118.5 (CH). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{48}H_{37}N_4$ $[M + H]^+$ 669.3013, found 669.3011.

General Procedure for the Synthesis of Arylquinazolines. A stirred mixture of the corresponding chloroquinazoline (0.5 mmol), the appropriate arylboronic acid (1 mmol, 1.5 mmol for 2,4-dichloroquinazoline), and $Pd(PPh_3)_4$ (0.005 mmol) in degassed aqueous 2 M sodium carbonate (2 mmol, 1 mL)/ethanol (1 mL)/toluene (15 mL) was heated under reflux for 24 h under a nitrogen atmosphere (48 h for 2,4-dichloroquinazoline). The reaction mixture was cooled and filtered, and EtAcO/water 1/1 (20 mL) was added. The organic layer was separated and the aqueous layer extracted with additional EtAcO (2 × 10 mL). The combined organic extracts were dried over $MgSO_4$ and the solvents evaporated under reduced pressure.

(*E*)-4-(4-Dimethylaminophenyl)quinazoline (9a). Purified by column chromatography (SiO_2, petroleum ether/EtAcO, 1/1). Yellow solid. Yield: 75% (93 mg). Mp: 114−115 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.99 (s, 6H), 6.76 (d, 2H, J = 8.7 Hz), 7.51−7.46 (m, 1H), 7.70 (d, 2H, J = 8.7 Hz), 7.77 (dt, 1H, J_1 = 8.1 Hz, J_2 = 1.2 Hz), 7.97 (d, 1H, J = 8.1 Hz), 8.18 (d, 1H, J = 8.1 Hz), 9.20 (s, 1H). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 168.0 (C), 154.7 (CH), 151.8 (C), 151.2 (C), 133.1 (CH), 131.7 (CH), 128.7 (CH), 127.5 (CH), 127.1 (CH), 124.5 (C), 123.1 (C), 111.7 (CH), 40.2 (CH_3). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{16}H_{15}N_3Na$ $[M + Na]^+$ 272.1164, found 272.1163.

(*E*)-4-(4-Diphenylaminophenyl)quinazoline (9b). Purified by column chromatography (SiO_2, petroleum ether/EtAcO, 7/3). Yellow solid. Yield: 81% (151 mg). Mp: 141−142 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.13−7.08 (m, 2H), 7.29−7.19 (m, 6H), 7.35−7.29 (m, 4H), 7.61 (dt, 1H, J_1 = 8.1 Hz, J_2 = 1.2 Hz), 7.70 (d, 2H, J = 8.7 Hz), 7.90 (dt, 1H, $J1$ = 8.1 Hz, J_2 = 1.2 Hz), 8.10 (d, 1H, J = 8.1 Hz), 8.26 (d, 1H, J = 8.1 Hz), 9.32 (s, 1H). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 168.0 (C), 154.7 (CH), 151.8 (C), 151.2 (C), 133.1 (CH), 131.7 (CH), 128.7 (CH), 127.5 (CH), 127.1 (CH), 124.5 (C), 123.1 (C), 111.7 (CH), 40.2 (CH_3). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{26}H_{20}N_3$ $[M + H]^+$ 374.1657, found 374.1658.

(*E,E*)-2,4-Bis(4-dimethylaminophenyl)quinazoline (10a). Purified by column chromatography (SiO_2, petroleum ether/EtAcO, 1/1). Yellow solid. Yield: 51% (93 mg). Mp: 169−170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.06 (s, 6H), 3.09 (s, 6H), 6.82 (d, 2H, J = 9.0 Hz), 6.88 (d, 2H, J = 9.0 Hz), 7.43 (dt, 1H, J_1 = 7.2 Hz, J_2 = 0.9 Hz), 7.78 (dt, 1H, J_1 = 7.2 Hz, J_2 = 0.9 Hz), 7.89 (d, 2H, J = 8.7 Hz), 8.02 (d, 1H, J = 8.4 Hz), 8.19 (d, 1H, J = 8.4 Hz), 8.59 (d, 2H, J = 9.0 Hz). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 167.5 (C), 160.5 (C), 152.4 (C), 152.0 (C), 151.7 (C), 132.8 (CH), 131.7 (CH), 129.9 (CH), 128.6 (CH), 127.3 (CH), 126.5 (C), 125.7 (C), 125.3 (CH), 121.2 (C), 111.73 (CH), 111.70 (CH), 40.3 (2 × CH_3). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{24}H_{25}N_4$ $[M + H]^+$ 369.2079, found 369.2077.

(*E,E*)-2,4-Bis(4-diphenylaminophenyl)quinazoline (10b). Purified by column chromatography (SiO_2, petroleum ether/EtAcO, 7/3) followed by crystallization from DCM/*n*-heptane. Yellow solid. Yield: 36% (110 mg). Mp: 84−88 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11−7.05 (m, 4H), 7.23−7.16 (m, 12H), 7.36−7.29 (m, 8H), 7.41 (dt, 1H, J_1 = 7.2 Hz, J_2 = 0.9 Hz), 7.71 (d, 2H, J = 8.7 Hz), 7.74 (dt, 1H, J_1 = 7.2 Hz, J_2 = 0.9 Hz), 7.99(d, 1H, J = 8.4 Hz), 8.12 (d, 1H, J = 8.4 Hz), 8.42 (d, 2H, J = 8.7 Hz). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 167.4 (C), 160.1 (C), 152.3 (C), 149.9 (C), 149.7 (C), 147.4 (C), 147.2 (C), 133.3 (CH), 132.0 (C), 131.4 (CH), 130.8 (C), 129.7 (CH), 129.5 (CH), 129.3 (CH), 129.0 (CH), 127.1 (CH), 126.3 (CH), 125.3 (CH), 125.0 (CH), 123.8 (CH), 123.4 (CH), 122.5 (CH), 121.9 (CH), 121.3 (C). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{44}H_{33}N_4$ $[M + H]^+$ 617.2700, found 617.2700.

General Procedure for the Synthesis of Arylethynylquinazolines. A suspension of the corresponding chloroquinazoline (1.0 mmol), $[Pd(PPh_3)_2Cl_2]$ (70 mg, 0.1 mmol), and CuI (10 mg 0.05 mol) in diisopropylamine (10 mL) was degassed three times in a pressure tube. The acetylene derivative (1.2 mmol) was then added. The mixture was heated at 70 °C for 15 h and then filtered, and the residue was washed with DCM. The filtrate was washed with saturated aqueous ammonium chloride (2 × 25 mL) and water (2 × 25 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure.

4-(4-Dimethylaminophenylethynyl)quinazoline (11a). Purified by column chromatography (SiO_2, petroleum ether/EtAcO, 1/1). Orange solid. Yield: 68% (185 mg). Mp: 115−116 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.05 (s, 6H), 6.69 (d, 2H, J = 8.7 Hz), 7.63 (d, 2H, J = 8.7 Hz), 7.69 (dt, 1H J_1 = 8.1 Hz, J_2 = 1.2 Hz), 7.90 (dt, 1H J_1 = 8.1 Hz, J_2 = 1.2 Hz), 8.02 (d, 1H, J = 8.4 Hz), 8.41 (d, 1H, J = 8.4 Hz), 9.24 (s, 1H). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 155.1 (CH), 153.3 (C), 151.4 (C), 150.0 (C), 134.3 (CH), 134.0 (CH), 128.6 (CH), 127.9 (CH), 126.7 (CH), 125.2 (C), 111.7 (CH), 107.1 (C), 102.4 (C), 85.0 (C), 40.1 (CH_3). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{18}H_{16}N_3$ $[M + H]^+$ 274.1339, found 274.1341.

4-(4-Diphenylaminophenylethynyl)quinazoline (11b). Purified by column chromatography (SiO_2, petroleum ether/EtAcO, 7/3). Yellow solid. Yield: 76% (302 mg). Mp: 155−156 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.05−7.03 (m, 2H), 7.18−7.10 (m, 6H), 7.34−7.29 (m, 4H), 7.57 (d, 2H, J = 8.7 Hz), 7.69 (dt, 1H J_1 = 8.1 Hz, J_2 = 1.2 Hz), 7.91 (dt, 1H J_1 = 8.1 Hz, J_2 = 1.2 Hz), 8.03 (d, 1H, J = 8.4 Hz), 8.39 (d, 1H, J = 8.4 Hz), 9.28 (s, 1H). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 155.0 (CH), 152.9 (C), 150.1 (C), 149.9 (C), 146.6 (C), 134.2 (CH), 133.8 (CH), 129.6 (CH), 128.7 (CH), 128.1 (CH), 126.6 (CH), 125.7 (CH), 125.3 (C), 124.4 (CH), 120.9 (CH), 112.7 (C), 100.4 (C), 85.2 (C). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{28}H_{20}N_3$ $[M + H]^+$ 398.1642, found 398.1644.

2-Chloro-4-(4-dimethylaminophenylethynyl)quinazoline (12). Purified by column chromatography (SiO_2, petroleum ether/EtAcO, 7/3) followed by crystallization from DCM/*n*-heptane. Orange solid. Yield: 70% (215 mg). Mp: 198−199 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.08 (s, 6H), 6.70 (d, 2H, J = 8.7 Hz), 7.63 (d, 2H, J = 8.7 Hz), 7.70 (dt, 1H J_1 = 8.1 Hz, J_2 = 1.2 Hz), 7.94−7.92 (m, 2H), 8.39 (d, 1H, J = 8.4 Hz). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 157.2 (C), 155.7 (C), 151.75 (C), 151.69 (C), 135.0 (CH), 134.7 (CH), 128.1 (CH), 127.8 (CH), 127.0 (CH), 123.6 (C), 111.6 (CH), 106.4 (C), 105.2 (C), 85.0 (C), 40.0 (CH_3). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{18}H_{15}{}^{35}ClN_3$ $[M + H]^+$ 308.0954, found 308.0950.

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4-(4-Dimethylaminophenylethynyl)-2-phenylquinazoline (13). Obtained according to the general procedure described above for the synthesis of arylquinazolines. Purified by column chromatography (SiO_2, petroleum ether/EtAcO, 7/3). Yellow solid. Yield: 93% (162 mg). Mp: 144−145 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.06 (s, 6H), 6.72 (d, 2H, J = 8.7 Hz), 7.54−7.51 (m, 3H), 7.68−7.63 (m, 3H), 7.88 (dt, 1H J_1 = 8.1 Hz, J_2 = 1.2 Hz), 8.07 (d, 1H, J = 8.4 Hz), 8.41 (d, 1H, J = 8.4 Hz), 8.64 (d, 2H, J = 8.1 Hz). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 160.9 (C), 153.6 (C), 151.3 (C), 150.8 (C), 138.1 (C), 134.2 (CH), 133.9 (CH), 130.4 (CH), 128.9 (CH), 128.7 (CH), 128.5 (CH), 127.3 (CH), 126.7 (CH), 123.8 (C), 111.7 (CH), 107.5 (C), 101.3 (C), 85.3 (C), 40.1 (CH_3). HRMS (ESI/ASAP, TOF): m/z calculated for $C_{24}H_{20}N_3$ $[M + H]^+$ 350.1652, found 350.1656.

■ ASSOCIATED CONTENT

Supporting Information

Figures giving ^{1}H NMR and ^{13}C NMR spectra for all compounds, plots of emission maxima versus $E_T(30)$, and changes in the absorption spectra of **5a**, **9a**, and **11a** with increasing concentrations of TFA. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail for S.A.: sylvain.achelle@univ-rennes1.fr.
*E-mail for J.R.-L.: julian.rodriguez@uclm.es.

Notes

The authors declare no competing financial interest.

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