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Synthesis and Photophysical Investigation of a Series of Push–Pull Arylvinyldiazine Chromophores

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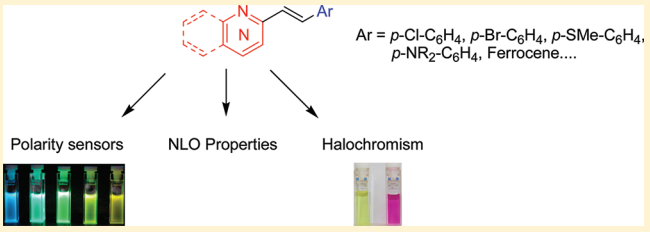
Supporting Information

ABSTRACT: A new series of push–pull arylvinyldiazines has been efficiently prepared by aldol condensation between the appropriate methyldiazine and aromatic aldehyde. The optical absorption and emission properties of these chromophores were studied in different solvents and media. These compounds act as polarity sensors with a strong positive emission solvatochromism. This behavior suggests a highly polar emitting state, which is characteristic of compounds that undergo an internal charge transfer upon excitation. These molecules also exhibit halochromic properties and are potential colorimetric and luminescence pH sensors. The second-order nonlinear properties have been investigated for some of the compounds, and large and positive $\mu\beta$ are obtained, in particular, for pyrimidine derivatives.



INTRODUCTION

Organic materials with extended π-conjugation along their backbone have received a lot of interest owing to their applications in a wide range of electronic and optoelectronic devices.[1] Organic molecules with large delocalized π-electron systems are also good candidates for the display of important fluorescence and large nonlinear responses.[2] One important factor involved in displaying such properties is the presence and nature of electron-donating and electron-accepting groups. Push–pull molecules, constituted of a conjugated π-electron system asymmetrically substituted by an electron-donor group and an electron-withdrawing one, is the typical structure of second-order nonlinear optic (NLO) chromophores.[3] Amino groups[4] and ferrocenyl moieties[5] have often been incorporated as organic or organometallic donors into push–pull assembled with NLO properties.

Diazines, which belong to the most important class of heterocycles containing nitrogen, are six-membered aromatics with two nitrogen atoms. Three different structures can be distinguished according to the relative positions of the nitrogen atoms: pyridazine (1,2-diazine),[6] pyrimidine (1,3-diazine),[7] and pyrazine (1,4-diazine).[8] The diazines with their highly π-deficient aromatic character are good candidates to be incorporated as electron-withdrawing groups into push–pull scaffolds favoring intramolecular charge transfer (ICT). The diazines allow protonation, hydrogen-bond formation, and chelation through the nitrogen atoms of the heterocycle; these are also of great importance since such derivatives could be, therefore, used for formation of supramolecular assemblies and used as sensors. Therefore, during the past two decades, pyridazine, pyrimidine, and pyrazine heterocycles have received intensive research interest as building blocks for the synthesis of functionalized π-conjugated materials.[9] In particular, star-shaped and bent-shaped structures with a pyrimidine central core substituted with electron-withdrawing groups exhibit intense fluorescence emission[10] and two photon absorption properties.[11] Linear structures incorporating pyrazine[12] or pyridazine[13] moieties exhibit also interesting emission properties, and V-shaped structures with a pyrazine central core have been also described in the literature as good fluorescent chromophores.[14] Benzodiazines, such as quinoxaline, have been also used as building blocks in the same context.[15] Surprisingly, only a few examples of second-order NLO chromophores incorporating diazines in their scaffold are described in the literature.[16]

The aim of the present article is to describe the synthesis of a series of new arylvinyldiazines and to compare their linear and nonlinear optical properties.

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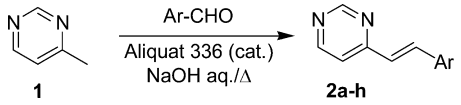
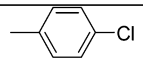
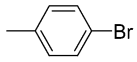
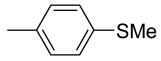
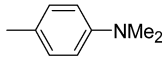
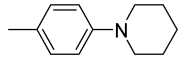
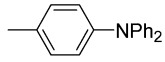
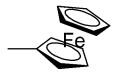
RESULTS AND DISCUSSION

Preparation of Arylvinyldiazines. Three main methods have been described for the synthesis of (*E*)-vinyldiazines:[17] The first consists of palladium-catalyzed cross-coupling reactions with halogenodiazines,[18] the second corresponds to Wittig or Horner–Wadsworth–Emmons reactions,[12b,c,13e] and the last is the condensation of aldehydes with methyldiazines.[19] The latter approach has the advantage of a wide range of commercially available aldehydes and, in most cases, the use of environmentally friendly conditions. In this way, 4-(arylvinyl)-pyrimidines **2a–2h** (Table 1) and 2-(arylvinyl)quinoxalines

Table 1. Condensation of 4-Methylpyrimidine with Aromatic Aldehydes



1 2a-h

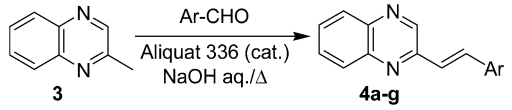
Compd	Ar	Isolated yield (%)
2a		77
2b		78
2c		59
2d		78
2e		67
2f		46
2g		18
2h		64

4a–4g (Table 2) have been obtained by condensation between aromatic aldehydes and the 4-methylpyrimidine (**1**) or the 2-methylquinoxaline (**3**), respectively, in boiling aqueous 5 M NaOH using Aliquat 336 as a phase-transfer catalyst. The experimental protocol is straightforward and offers easy access, in moderate to good yields, to a wide variety of 4-(arylvinyl)pyrimidines and 2-(arylvinyl)quinoxalines containing electron-donating groups. It should be noted that, due to a lower reactivity caused by a less favorable position of one of the two nitrogen atoms, 2-methylquinoxaline **3** requires a longer reaction time (15 h) in comparison with 4-methylpyrimidine **1**.

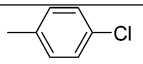
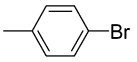
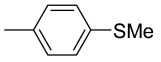
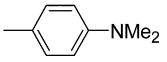
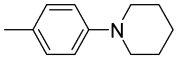
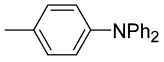
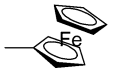
For the same reason, this method cannot be applied to 2-methylpyrazine **5** and 3-methylpyridazine **7**: more extreme conditions with potassium *tert*-butoxyde in refluxing THF are required to obtain 2-arylvinylpyrazines **6a**, **6b** (Scheme 1) and 3-arylvinylpyridazine **8** (Scheme 2).

To increase the electronic delocalization along the skeleton of the push–pull structures, tricyclic linear oligomers **9a–9c** and **10a–10c** were also synthesized in good yields by Suzuki cross-coupling[20] of bromo derivatives **2b** and **4b**, respectively, with the appropriate boronic acid (Scheme 3).

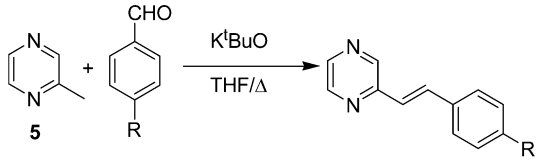
Table 2. Condensation of 2-Methylquinoxaline with Aromatic Aldehydes



3 4a-g

Compd	Ar	Isolated yield (%)
4a		51
4b		55
4c		24
4d		78
4e		42
4f		45
4g		45

Scheme 1. Condensation of 2-Methylpyrazine with Aromatic Aldehydes



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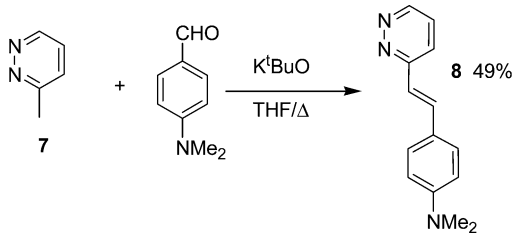
6a R = NMe_2 26%
6b R = NPh_2 34%

Scheme 2. Condensation of 2-Methylpyridazine with Aromatic Aldehydes



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Scheme 3. Suzuki Cross-Coupling Reaction of Bromo Derivatives 2b and 4b

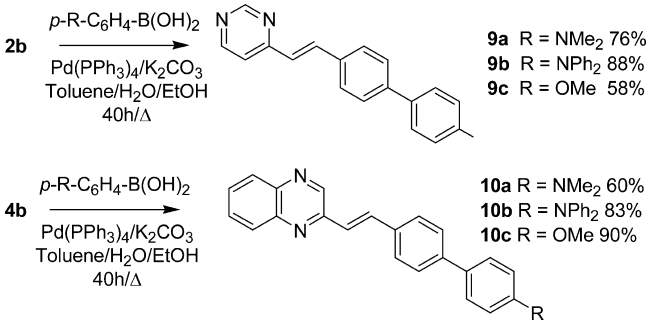

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Table 3. UV/vis and Photoluminescence (PL) Data

compd[a]	UV/vis λ_{max}, nm (ε, $M^{-1}\cdot cm^{-1}$)	PL λ_{max}, nm	Φ_F[b]	Stokes shift cm^{-1}
2a	226 (6200), 310(11 700)	411	<0.01	7927
2b	226 (6000), 317 (11 800)	410	<0.01	7155
2c	246 (15 800), 346 (23 200)	435	<0.01	5913
2d	255 (8900), 393 (28 600)	488	0.15	4953
2e	257 (10 800), 386 (28 000)	498	0.13	5826
2f	226 (17 600), 289 (19 900), 400 (32 000)	526	0.45	5989
2g	227 (4000), 337 (18 900)	401	<0.01	4736
2h	322 (15 100), 482 (1700)	614	<0.01	4460
4a	294 (12 200), 355 (11 400)	416	<0.01	4130
4b	276 (93 600), 369 (13 400)	455	0.02	5122
4c	257 (12 500), 286 (12 800), 381 (21 600)	475	0.02	5194
4d	228 (15 900), 305 (12 300), 427 (22 400)	570	0.59	5875
4e	227 (17 400), 302 (14 500), 414 (25 200)	583	0.70	7001
4f	227 (18 800), 307 (18 800), 427 (25 400)	565	0.67	5720
4g	227 (17 100), 336 (13 100), 502 (3000)	624	<0.01	3895
6a	266 (8300), 389 (19 000)	511	0.17	6137
6b	232 (12 800), 296 (19 000), 394 (23 500)	532	0.41	6584
8	250 (13 800), 365 (16 500)	480	0.02	6564
9a	296 (24 600), 386 (32 400)	570	0.66	8362
9b	304 (34 400), 384 (35 400)	563	0.52	8280
9c	227 (18 000), 346 (33 200)	447	0.14	6530
10a	312 (32 200), 406 (43 700)	617	0.14	8792
10b	310 (32 500), 393 (36 400)	632	0.35	9623
10c	296 (20 400), 379 (29 900)	485	0.42	5767

[a]All spectra were recorded in CH_2Cl_2 solutions at room temperature at $c = 1.0 \times 10^{-5}$ to 3.0×10^{-5} M for absorption and $c = 1.0 \times 10^{-6}$ to 3.0×10^{-6} M for emission. [b]Fluorescence quantum yield (±10%) determined relative to quinine sulfate in 1 M H_2SO_4 ($\Phi_F = 0.54$) or harmane in 0.1 M H_2SO_4 as standard ($\Phi_F = 0.83$).

All new compounds are soluble in THF, chloroform, and dichloromethane and were characterized using a variety of analytical techniques. The overall purities of these products were confirmed by elemental analysis. NMR experiments proved very usefull to confirm the structures of the compounds (see the Experimental Section and Supporting Information). The selectivity of the aldol reactions was sufficiently high to generate all-trans isomers within the limits of NMR detection. The stereochemistry of the double bonds was unequivocally established on the basis of the coupling constant for the vinylic protons in the ^1H NMR spectra ($J \approx 16$ Hz).

These materials are perfectly stable in the solid state and could be stored without the need for 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 PL Spectroscopy. The UV−vis and photoluminescence (PL) spectroscopic data of various oligomers measured in dichloromethane at 25 °C are presented in Table 3. Analyses have been carried out using low concentration solutions (1.0×10^{-5} to 3.0×10^{-5} M for UV/vis spectra and 1.0×10^{-6} to 3.0×10^{-6} M for PL spectra). As an example, the spectra for derivatives **2d**, **3e**, and **9c** are shown in Figure 1. Under these conditions, self-absorption effects were not observed. All compounds are photostable and did not undergo cis−trans isomerization under the analysis conditions.

All compounds show absorption wavelengths (λ_{max}) in the UV or visible region (310−482 nm). In some cases, a second or even a third absorption band of higher energy can be observed, a situation in agreement with calculated and experimental results for related structures.[10g] An MLCT (metal-to-ligand charge transfer) band is observed for ferrocenyl derivatives **2h** and **4g**. All compounds are fluorescent. In general, large Stokes shifts were obtained for the compounds under investigation. As observed in related structures,[8] this phenomenon indicates large differences (vibrational, electronic, geometric) between the Franck−Condon state and the excited state.

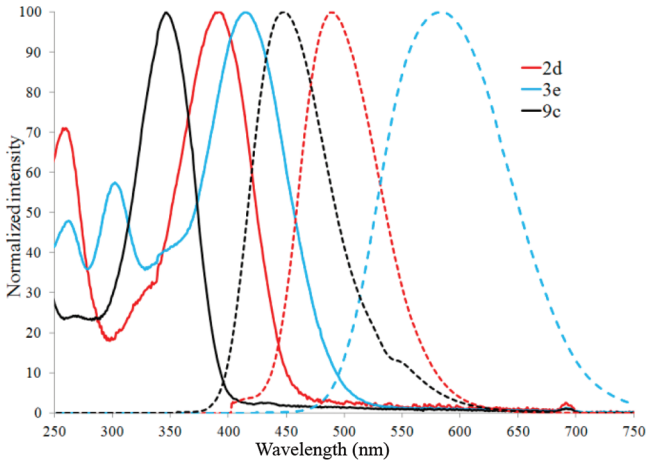

Figure 1. Normalized UV/vis (solid line) and emission spectra (broken line) of compounds **2d**, **3e**, and **9c**.

Pyrimidine derivatives **2** and **9**, when compared to already described[10d] symmetrically disubstituted derivatives, show slightly low absorption and emission wavelengths and the absorption coefficient lowered with a factor of about 2. Quantum yields are also slightly lower. Photophysical properties of pyrazine derivatives (compounds **6**) are similar to those of pyrimidine derivatives **2**. Comparison of quinoxaline

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derivatives **4** with other diazine derivatives **2**, **6**, and **8** showed a bathochromic shift and higher quantum yields.

Compounds **9a**, **9b** and **10a**, **10b** (with a biphenyl unit) have higher values of λ_{em}, and ε than analogous compounds **2d**, **2f** and **4d**, **4f** (with only one benzene ring per arm) due to extension of the conjugation. As far as the fluorescence quantum yield is concerned, a dramatic increase was observed in the case of pyrimidine derivatives **9a**, **9b**, whereas quinoxaline compounds **10a**, **10b** had lower Φ_F values than derivatives **4d**, **4f**, probably due to more effective aggregation. When the position of the lowest-energy absorption band of the quinoxaline derivatives is plotted versus the position of the same band for the pyrimidine derivatives (Figure 2), an

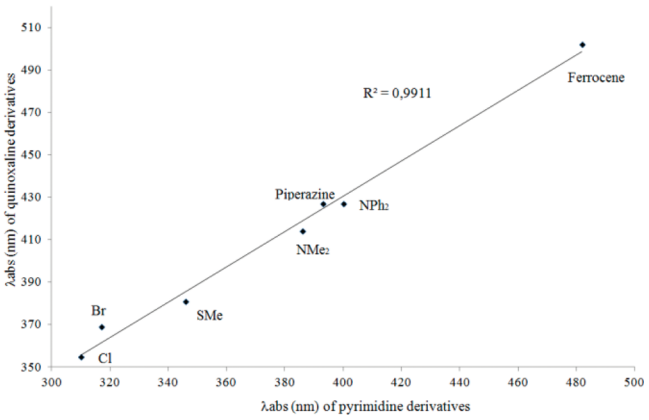

Figure 2. Position of the lower-energy absorption band for the quinoxaline derivatives versus the position of the lower-energy absorption band for the pyrimidine derivatives.

excellent correlation coefficient is observed (R^2 = 0.99). This indicates that the electronic factors of the substituent acts in the same way in the electronic transition. The point corresponding to the ferrocene derivatives (**2h** and **4g**) is aligned with the other points, which could indicate that the HOMO has partial π character.

In an effort to gain further insight into the photophysical process within these push–pull molecules, we investigated both the absorption and the emission behaviors of **2e**, **2f**, **4c**–**4f**, **6b**, **8**, and **9b** in different aprotic solvants. The results of these investigations are summarized in Table 4, and emission maxima have been plotted versus $\Delta E_T(30)$ (see the Supporting Information, S27 and S28). For all compounds, a bathochromic shift of the emission band is observed with increasing solvent polarity, as predicted by the Dimroth–Reichardt polarity parameter.[21] In contrast, the absorption wavelength is not significantly shifted. Broad structureless emission and larger Stokes shifts were observed for polar solvents. This solvatochromic behavior, which results from the stabilization of the highly polar emitting state by polar solvents, is typical for compounds exhibiting an internal charge transfer upon excitation and has been fully documented with donor–acceptor fluorophores.[22] As an example, the PL spectra for compound **4d** and color change under UV irradiation for compound **2f** are shown in Figures 3 and 4.

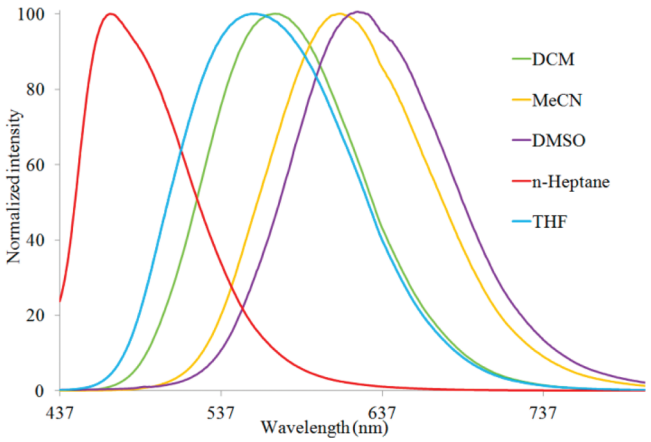

Figure 3. Normalized emission of compound **4d** in various solvents.

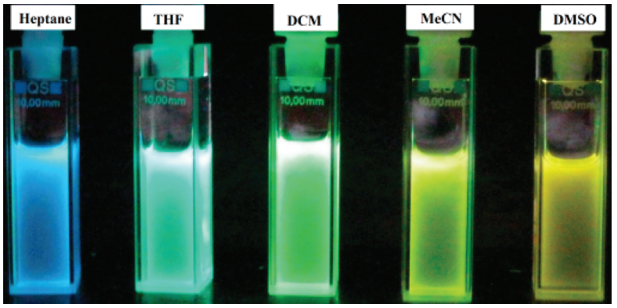

Figure 4. Color of solutions of **2f** in various solvents (c = 10^{-3} M).

When comparing the quinoxaline derivatives, the dimethylamino-substituted compound **4d** shows the higher emission

Table 4. Optical Properties of Arylvinyldiazines 2e, 2f, 4c–4f, 6a, 8, and 9b in Various Aprotic Solvents

	n-heptane $\Delta E_T(30)^a$ = 0.0		THF $\Delta E_T(30)^a$ = 27.2		CH_2Cl_2 $\Delta E_T(30)^a$ = 42.7		acetonitrile $\Delta E_T(30)^a$ = 58.6		DMSO $\Delta E_T(30)^a$ = 59.0	
compd	UV/vis λ_{max}, nm	PL λ_{max}, nm	UV/vis λ_{max}, nm	PL λ_{max}, nm	UV/vis λ_{max}, nm	PL λ_{max}, nm	UV/vis λ_{max}, nm	PL λ_{max}, nm	UV/vis λ_{max}, nm	PL λ_{max}, nm
2e	375	435	381	486	386	498	378	514	389	521
2f	392	443	398	496	400	526	394	545	401	550
4c	373	426	376	467	381	475	377	499	383	513
4d	418	468	424	556	427	570	424	611	435	622
4e	402	480	410	557	414	583	410	617	423	626
4f	416	461	423	535	427	565	425	596	436	598
6b	386	433	393	487	394	532	391	535	400	537
8	361	459	369	476	365	480	369	509	380	518
9b	373	445	381	525	384	563	381	599	393	609

[a]Dimroth–Reichardt polarity parameter (kJ·mol^{-1}).

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solvatochromic range ($\Delta\lambda$ = 154 nm, $\Delta\nu$ = 5290 cm^{-1}), compared with the diphenylamino derivative **4f** ($\Delta\lambda$ = 137 nm, $\Delta\nu$ = 4969 cm^{-1}), which is in accordance with values found in the literature, indicating that the diphenylamino substituent has a less electron-donating character than the dimethylamino group.[23] When comparing compounds **2f** ($\Delta\lambda$ = 107 nm, $\Delta\nu$ = 4391 cm^{-1}), **4f**, and **6b** ($\Delta\lambda$ = 104 nm, $\Delta\nu$ = 4472 cm^{-1}), it appears that the quinoxaline is the most electron-attracting heterocycle of the series. As expected, the biphenyl derivative **9b** ($\Delta\lambda$ = 164 nm, $\Delta\nu$ = 6051 cm^{-1}) exhibits a more important charge transfer than its analogue with only one phenyl ring (**2f**).

In previous studies,[10d,e] we demonstrated the ability of related 4,6-bis(arylvinyl)pyrimidines and 4-arylvinyl-2,6-di-(pyridine-2-yl)pyrimidines to function as colorimetric and luminescent pH sensors due to the basic character of the nitrogen atoms of the pyrimidine ring. For this reason, we decided to study the effect of protonation on the optical properties of several of the prepared arylvinyldiazines (**2c**–**2f**, **2h**, **4a**, **4c**–**4g**, **6a**, **8**, **9c**, **10c**). Dichloromethane solutions of these compounds underwent a significant color change in the presence of TFA (10^{-2} M) (Table 5, Figures 5–7). This color change is fully reversible by neutralization with a base, such as Et_3N or KBu^tO. As expected, most of the compounds exhibit a bathochromic shift of their absorption and emission bands upon addition of TFA (10^{-2} M). The bathochromic shifts of the absorption can be explained by an increased charge transfer from the donors to the diazinium moiety. However, surprisingly, for compounds bearing a piperidyl amino group (**2e** and **4e**) as well as pyrazine and pyridazine derivatives bearing a dimethylamino group (**6a** and **8**), an hypsochromic shift of the absorption band is observed upon addition of TFA (10^{-2} M). It may be due to the protonation of the amino groups. For most of the protonated species, the emission is partially or totally quenched; however, compounds **2c** and **4c** exhibit a more intense and red shifted emission after protonation. Ferrocenyl derivatives **2h** and **4g** become nonemissive after protonation. Even if this study has been carried out in an organic solvent with a strong organic acid, a recent study has shown that pyrimidine chromophores can be incorporated in pluronic nanoparticules and used as pH sensors in aqueous media.[24]

Table 5. Optical Properties of Arylvinyldiazines 2c, 2d, 2f, 2h, 4d, 6a, 8a, and 9c upon Addition of TFA

compd[a]	UV/vis (TFA 10^{-2} M in DCM) λ_{max}, nm (ε, $M^{-1}\cdot cm^{-1}$)	PL λ_{max}, nm	Stokes shift cm^{-1}
2c	439 (23 000)	551	4630
2d	523 (23 100)	601	2482
2e	345 (43 500)	405	4294
2h	568 (2200)	[b]	[b]
4a	421 (18 700)	504	3912
4c	485 (15 300)	630	4746
4d	584 (10 300)	450	3685
4e	406 (56 400)	473	3488
4f	579 (29 400)	[b]	[b]
4g	670 (6200)	[b]	[b]
6a	325 (13 000)	[b]	[b]
8	311 (25 800)	426	8680
9a	426 (15 800)	594	6639

[a]All spectra were recorded at room temperature at $c = 6.3 \times 10^{-6}$ M to 1.3×10^{-5} M. [b]No fluorescence.

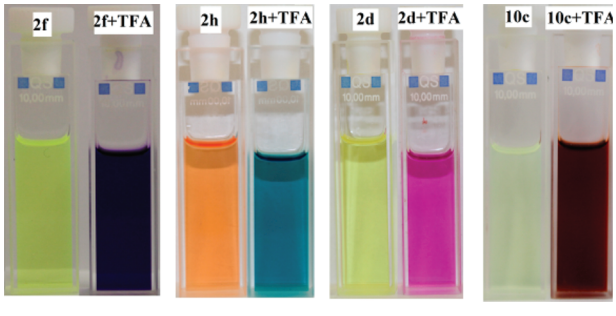

Figure 5. Color change of CH_2Cl_2 solutions of several arylvinyldiazines (c = 10^{-3} M in the presence of 10^{-2} M TFA).

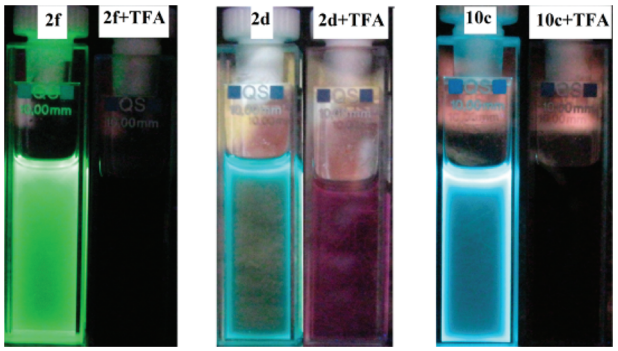

Figure 6. Color change of CH_2Cl_2 solutions of several arylvinyldazines (c = 10^{-3} M in the presence of 10^{-2} M TFA under UV irradiation).

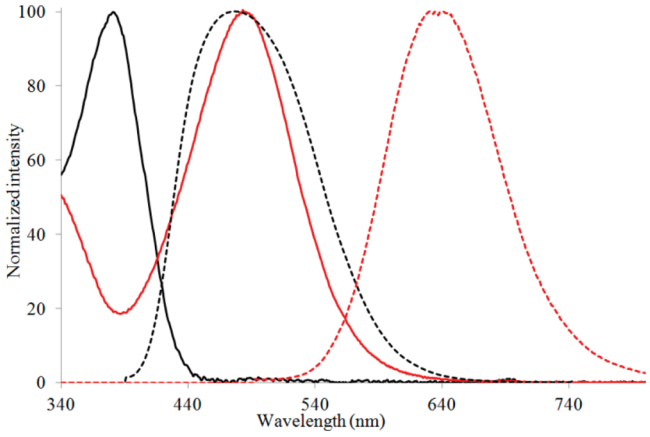

Figure 7. Normalized UV/vis and PL spectra of **2c** in CH_2Cl_2 (c = 10^{-5} M) with (red) and without (black) addition of TFA.

Second-Order Nonlinear Optical Properties. Second-order nonlinear properties have been studied in $CHCl_3$ solution by the electric-field-induced second-harmonic generation technique (EFISH), which provides information about the scalar product $\mu\beta$ (2ω) of the vector component of the first hyperpolarizability tensor β and the dipole moment vector.[25] This product is derived according to eq 1 and, considering $\gamma_0(-2\omega,\omega,\omega,0)$, the third-order term, is negligible for the push–pull compounds under study. This approximation is usually used for push–pull organic and organometallic molecules.

$$\gamma_{EFISH} = \mu\beta/5kT + \gamma_0(-2\omega,\omega,\omega,0) \quad (1)$$

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Measurements are performed at 1907 nm, obtained from a Raman-shifted Nd:YAG$^+$ laser source, which allows us to work far from the resonance peaks of the compounds we investigated (**2d**−**2f**, **2h**, **4d**, **6a**, **8**, and **9a**). For push−pull molecules, according to the two-level approximation, the static quadratic hyperpolarizability β_0 (and concomitantly β) is expected to increase with decreasing the internal charge-transfer (ICT) transition energy E_0, with increasing the transition dipole moment μ_0 and change in dipole moment $\Delta\mu_0$ upon excitation ($\Delta\mu_0$ being the difference between excited-state and ground-state dipole moments) (eq 2).

$$\beta_0 = \frac{3\mu_0\Delta\mu_0}{2E_0^{\,2}} \qquad (2)$$

In addition, theoretical studies have shown that the NLO response is correlated to the ground-state polarization and concomitantly with the bond length alternation of adjacent carbon−carbon bonds of the π-conjugated system (Figure 8).[26]

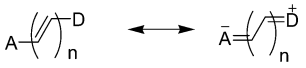

Figure 8. Resonance structure of push−pull molecules.

Minimum and maximum β values are reached for a zwitterionic molecular structure and a structure standing between the neutral and zwitterionic form, respectively.

It should be noted that the sign and values of $\mu\beta$ depend on the "direction" of the transition implied in the NLO phenomena and on the direction of the ground-state dipole moment. When β and μ are parallel (antiparallel), positive (negative) maxima $\mu\beta$ values are reached.

All the $\mu\beta$ values of compounds **2d**−**2f**, **2h**, **4d**, **6a**, **8**, and **9a** (Table 6) are positive, indicative of excited states, which are more polarized than the ground state ($\mu_e > \mu_g$). In addition, this implies that the ground and excited states are polarized in the same direction. The positive values are in accordance with the emission solvatochromism observed for the compounds (Table 4). The $\mu\beta$ values observed are similar to Disperse Red 1, as measured in the literature.[27] It should be noted that $\mu\beta$ values might be slightly underestimated due to possible aggregation at the concentration used.

Table 6. $\mu\beta$ Values for Compounds 2d−2f, 2h, 4d, 6a, 8, and 9a

	2d	2e	2f	2h	4d	6a	8	9a
$\mu\beta$ [10^{-48} esu][a]	330	290	190	160	300	220	210	470

[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. $\mu\beta$ ± 10%.

When comparing the pyrimidine compounds **2d**−**2f** and **2h**, it appears that the dimethylamino and piperidine derivatives **2d** and **2e** gave the better second-order NLO answer. In compound **2f**, the presence of the diphenylamino group decreases the $\mu\beta$ value despite the fact that this group lowers the ICT energy (Table 3). This observation should be the consequence of the low delocalization of the amino electron pair (lower donor strength, which shifts the ground-state structure to a less favorable bond alternation). In our case, the favorable effect the polarizable nature of the phenyl substituents is inoperative.[28]

The presence of a ferrocenyl group in compound **2h** gave the lower $\mu\beta$ value, in accordance with a donor strength for the ferrocenyl part comparable to that of a *p*-methoxyphenyl group.[29] It should be noted that, in this case, the MLCT plays a partial role in the NLO phenomena.[30]

As usually observed in push−pull compounds, lengthening the π-spacer favors the NLO responses: a significant increase of the $\mu\beta$ value is observed when going from a phenyl π-conjugated spacer (compound **2d**) to a biphenyl one (compound **9a**). The comparison of pyrimidine (compound **2d**) and quinoxaline (**4d**) with pyrazine (**6a**) and pyridazine (**8**) as the attracting part in the push−pull structures indicates that the better $\mu\beta$ values are observed for the first pair of compounds. This is in accordance with the higher reactivity of 4-methylpyrimidine and 2-methylquinoxaline compared with that of the two other diazines, indicating that the pyrimidine and quinoxaline heterocycles are more electron-attracting than the other diazines. It is noteworthy that, in accordance with the two-level model, the pyridazine **8**, which gave the lower NLO answer of the series, displays the higher transition energy and the weaker absorption coefficient ε (Table 3) directly related to the transition dipole moment μ_0.

CONCLUSIONS

In conclusion, we have successfully synthesized and characterized a series of push−pull arylvinyldiazines in a straightforward manner by aldol condensation between the appropriate methyldiazines and aromatic aldehydes. The resulting compounds were characterized using a variety of techniques. The optical properties were studied: all of the molecules present absorption wavelengths in the UV or visible region and emit light with significant Stokes shifts. The quinoxaline derivatives give the most red shifted emission and the highest fluorescence quantum yields. The results of solvatochromism studies support the formation of very polar excited intramolecular charge-transfer states with terminal electron-donating groups. Likewise, these arylvinyldiazines display a dramatic and reversible color change and luminescence switching upon addition of acid. This phenomenon is due to the protonation of the nitrogen atoms of the diazine ring. This behavior indicates that this type of material is valuable for the development of colorimetric and luminescent pH sensors. The second-order nonlinear properties have been investigated for some of the compounds, and large and positive $\mu\beta$ are obtained, in particular, for pyrimidine derivatives. Investigations are currently carried out to complex metals to the diazine ring, so as to increase its electron-attracting character and to enlarge the π-conjugated spacer.

EXPERIMENTAL SECTION

General. In 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) for recording the emission spectra; however different wavelengths were used to determine fluorescence quantum yields in cases where compounds and standards absorbed significantly. All solutions were measured with optical densities below 0.1. Stokes shifts were calculated considering the lowest energetic absorption band.

General Procedure for the Synthesis of 4-Arylvinylpyrimidines. A stirred mixture of 4-methylpyrimidine (94 mg, 1 mmol) and

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the corresponding aldehyde (0.9 mmol) in aqueous sodium hydroxide (5 M, 15 mL) containing Aliquat 336 (43 mg, 0.1 mmol) was heated under reflux for 2 h. The mixture was allowed to cool, and the precipitate was filtered off, washed with water, and purified by column chromatography (SiO_2) and/or by recrystallization from the indicated solvent.

*4-[2-(4-Chloro-phenyl)-vinyl]-pyrimidine (**2a**):* Pale pink solid; purified by crystallization from a mixture of CH_2Cl_2/*n*-heptane; 150 mg; yield 77%; mp 116−117 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (d, 1H, J = 16 Hz), 7.28 (d, 1H, J = 5 Hz), 7.35 (d, 2H, J = 8 Hz), 7.50 (d, 2H, J = 8 Hz), 7.83 (d, 1H, J = 16 Hz), 8.66 (d, 1H, J = 5 Hz), 9.15 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 161.9 (C), 158.9 (CH), 157.5 (CH), 136.1 (CH), 135.3 (C), 134.1 (CH), 129.2 (CH), 128.9 (CH), 126.1 (C), 118.8 (CH). Anal. Calcd for $C_{12}H_9ClN_2$: C, 66.52; H, 4.19; N, 12.93. Found: C, 66.35; H, 4.52; N, 12.53.

*4-[2-(4-Bromo-phenyl)-vinyl]-pyrimidine (**2b**):* Pale pink solid; purified by crystallization from a mixture of CH_2Cl_2/*n*-heptane; 184 mg; yield 78%; mp 120−121 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (d, 1H, J = 16 Hz), 7.28 (d, 1H, J = 5 Hz), 7.44 (d, 2H, J = 8 Hz), 7.52 (d, 2H, J = 8 Hz), 7.81 (d, 1H, J = 16 Hz), 8.67 (d, 1H, J = 5 Hz), 9.16 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 161.9 (C), 158.9 (CH), 157.6 (CH), 136.1 (CH), 134.5 (C), 132.1 (CH), 129.1 (CH), 126.2 (CH), 123.6 (C), 118.9 (CH). Anal. Calcd for $C_{12}H_9BrN_2$: C, 55.20; H, 3.47; N, 10.73. Found: C, 55.57; H, 3.87; N, 10.81.

*4-[2-(4-Thiomethyl-phenyl)-vinyl]-pyrimidine (**2c**):* Cream solid; purified by crystallization from a mixture of CH_2Cl_2/*n*-heptane; 121 mg; yield 59%; mp 103−104 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.51 (s, 3H), 7.00 (d, 1H, J = 16 Hz), 7.26 (d, 1H, J = 5 Hz), 7.27 (d, 2H, J = 8 Hz), 7.50 (d, 2H, J = 8 Hz), 7.83 (d, 1H, J = 16 Hz), 8.65 (d, 1H, J = 5 Hz), 9.14 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 162.3 (C), 158.9 (CH), 157.3 (CH), 140.8 (C), 136.8 (CH), 132.2 (C), 128.1 (CH), 126.2 (CH), 124.6 (CH), 118.6 (CH), 15.3 (CH_3); Anal. Calcd for $C_{13}H_{12}N_2S$: C, 68.39; H, 5.30; N, 12.27; S, 14.04. Found: C, 68.28; H, 5.33; N, 12.07; S, 13.89.

*4-[2-(4-N,N-Dimethylamino-phenyl)-vinyl]-pyrimidine (**2d**):* Yellow solid; purified by crystallization from a mixture of CH_2Cl_2/*n*-heptane; 158 mg; yield 78%; mp 176−177 °C (lit.[31] 179 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.03 (s, 6H), 6.71 (d, 2H, J = 8 Hz), 6.84 (d, 1H, J = 16 Hz), 7.24 (d, 1H, J = 5 Hz), 7.50 (d, 2H, J = 8 Hz), 7.81 (d, 1H, J = 16 Hz), 8.58 (d, 1H, J = 5 Hz), 9.09 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 163.1 (C), 158.8 (CH), 156.8 (CH), 151.3 (C), 137.9 (CH), 129.3 (CH), 123.5 (C), 120.5 (CH), 117.9 (CH), 112.0 (CH), 40.2 (CH_3); Anal. Calcd for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.38; H, 6.56; N, 18.81.

*4-[2-(4-Piperidin-1-yl-phenyl)-vinyl]-pyrimidine (**2e**):* Yellow solid; purified by crystallization from a mixture of CH_2Cl_2/*n*-heptane; 160 mg; yield 67%; mp 161−162 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.64−1.62 (m, 2H), 1.72−1.67 (m, 4H), 3.29−3.27 (m, 4H), 6.87 (d, 1H, J = 16 Hz), 6.90 (d, 2H, J = 8 Hz), 7.27 (d, 1H, J = 5 Hz), 7.49 (d, 2H, J = 8 Hz), 7.80 (d, 1H, J = 16 Hz), 8.59 (d, 1H, J = 5 Hz), 9.10 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 163.0 (C), 157.0 (CH), 152.6 (C), 137.7 (CH), 129.1 (2 × CH), 125.4 (C), 121.5 (CH), 118.1 (CH), 115.2 (CH), 49.4 (CH_2), 25.6 (CH_2), 24.4 (CH_2); Anal. Calcd for $C_{17}H_{19}N_3$: C, 76.95; H, 7.22; N, 15.84. Found: C, 77.23; H, 7.20; N, 15.56.

*4-[2-(4-N,N-Diphenylamino-phenyl)-vinyl]-pyrimidine (**2f**):* Yellow solid; purified by column chromatography (SiO_2, CH_2Cl_2/EtAcO, 7:3); 145 mg; yield 46%; mp 151−152 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91 (d, 1H, J = 16 Hz), 7.04 (d, 2H, J = 8 Hz), 7.08 (t, 2H, J = 7 Hz), 7.13 (d, 4H, J = 7.5 Hz), 7.30−7.26 (m, 5H), 7.45 (d, 2H, J = 8 Hz), 7.82 (d, 1H, J = 16 Hz), 8.62 (d, 1H, J = 5 Hz), 9.13 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 162.6 (C), 158.9 (CH), 157.2 (CH), 149.2 (C), 147.1 (C), 137.1 (CH), 129.5 (CH), 128.9 (C), 128.8 (CH), 125.2 (CH), 123.82 (CH), 123.78 (C), 123.1 (CH), 122.2 (CH), 118.4 (CH). Anal. Calcd for $C_{24}H_{19}N_3$: C, 82.49; H, 5.48; N, 12.03. Found: C, 82.76; H, 5.55; N, 11.67.

*4-(2-Furan-2-yl-vinyl)-pyrimidine (**2g**):* Pale yellow solid; purified by column chromatography (SiO_2, CH_2Cl_2/EtAcO, 7:3); 28 mg; yield 18%; mp 72−73 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.48 (dd, 1H, J_1 = 3.5 Hz, J_2 = 2 Hz), 6.58 (d, 1H, J_1 = 3.5 Hz,), 6.94 (d, 1H, J = 16 Hz), 7.21 (d, 1H, J = 5 Hz), 7.49 (d, 1H, J = 2 Hz), 7.71 (d, 1H, J = 16 Hz), 8.64 (d, 1H, J = 5 Hz), 9.12 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 162.0 (C), 158.8 (CH), 157.4 (CH), 152.1 (C), 144.1 (CH), 124.3 (CH), 123.3 (CH), 119.0 (CH), 113.3 (CH), 112.3 (CH); Anal. Calcd for $C_{10}H_8N_2O$: C, 69.76; H, 4.68; N, 16.27. Found: C, 69.70; H, 4.88; N, 16.02.

*4-(Ferrocenyl-vinyl)-pyrimidine (**2h**):* Red solid; purified by crystallization from a mixture of CH_2Cl_2/*n*-heptane; 167 mg: yield 64%; mp 135−136 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.18 (s, 5H), 4.43 (s, 2H), 4.57 (s, 2H), 6.65 (d, 1H, J = 16 Hz), 7.21 (d, 1H, J = 5 Hz), 7.75 (d, 1H, J = 16 Hz), 8.62 (s br, 1H), 9.11 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 162.5 (C), 158.7 (CH), 156.9 (CH), 138.3 (CH), 122.5 (CH), 117.8 (CH), 80.4 (C), 70.6 (CH), 69.6 (CH), 68.2 (CH); HRMS (ESI$^+$, TOF) m/z calculated for $C_{16}H_{15}N_2Fe$, 291.0585; found, 291.0598.

General Procedure for the Synthesis of 2-Arylvinylquinoxalines. A stirred mixture of 2-methylquinoxaline (288 mg, 2 mmol) and the corresponding aldehyde (1 mmol) in aqueous sodium hydroxide (5 M, 15 mL) containing Aliquat 336 (43 mg, 0.1 mmol) was heated under reflux for 15 h. The mixture was allowed to cool, and the precipitate was filtered off, washed with water, and purified by column chromatography (SiO_2) and/or by recrystallization from the indicated solvent.

*2-[2-(4-Chloro-phenyl)-vinyl]-quinoxaline (**4a**):* Pale pink solid; purified by column chromatography (SiO_2, CH_2Cl_2/EtAcO, 8:2) and crystallization from a mixture of CH_2Cl_2/*n*-heptane; 136 mg; yield 51%; mp 140 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, 1H, J = 16 Hz), 7.40 (d, 2H, J = 8 Hz), 7.60 (d, 2H, J = 8 Hz), 7.74−7.71 (m, 1H), 7.79−7.76 (m, 1H), 7.84 (d, 1H, J = 16 Hz), 8.10−8.06 (m, 2H), 9.03 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 150.3 (C), 144.5 (CH), 142.5 (C), 141.7 (C), 135.0 (CH), 134.6 (C), 130.4 (CH), 129.5 (CH), 129.2 (CH), 129.1 (CH), 128.6 (CH), 125.8 (CH), 123.3 (CH). Anal. Calcd for $C_{16}H_{11}ClN_2$: C, 72.05; H, 4.16; N, 10.50. Found: C, 72.07; H, 3.98; N, 10.33.

*2-[2-(4-Bromo-phenyl)-vinyl]-quinoxaline (**4b**):* Pale pink solid; purified by column chromatography (SiO_2, CH_2Cl_2/EtAcO, 8:2); 171 mg; yield 55%; mp 153−154 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, 1H, J = 16 Hz), 7.51 (d, 2H, J = 8 Hz), 7.55 (d, 2H, J = 8 Hz), 7.73−7.70 (m, 1H), 7.79−7.75 (m, 1H), 7.81(d, 1H, J = 16 Hz), 8.08−8.05 (m, 2H), 9.01 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 150.3 (C), 144.5 (CH), 142.5 (C), 141.7 (C), 135.1 (CH), 135.0 (C), 132.1 (CH), 130.5 (CH), 129.5 (2 × CH), 129.2 (CH), 128.9 (CH), 125.9 (CH), 123.3 (C). Anal. Calcd for $C_{16}H_{11}BrN_2$: C, 61.78; H, 3.56; N, 9.00. Found: C, 61.70; H, 3.59; N, 8.70.

*2-[2-(4-Thiomethyl-phenyl)-vinyl]-quinoxaline (**4c**):* Pale pink solid; purified by column chromatography (SiO_2, CH_2Cl_2/EtAcO, 8:2) and crystallization from a mixture of CH_2Cl_2/*n*-heptane; 67 mg; yield 24%; mp 105−106 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.53 (s, 3H), 7.27 (d, 2H, J = 8 Hz), 7.33 (d, 1H, J = 16 Hz), 7.58 (d, 2H, J = 8 Hz), 7.72−7.68 (m, 1H), 7.77−7.74 (m, 1H), 7.83 (d, 1H, J = 16 Hz), 8.08−8.05 (m, 2H), 9.02 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 150.7 (C), 144.5 (CH), 142.5 (C), 141.6 (C), 140.4 (C), 135.8 (CH), 132.7 (C), 130.3 (CH), 129.2 (2 × CH), 129.1 (CH), 127.9 (CH), 126.3 (CH), 124.5 (CH). Anal. Calcd for $C_{17}H_{14}N_2S$: C, 73.35; H, 5.07; N, 10.06; S, 11.52. Found: C, 73.35; H, 5.22; N, 9.61; S, 11.39.

*2-[2-(4-N,N-Dimethylamino-phenyl)-vinyl]-quinoxaline (**4d**):* Yellow solid; purified by crystallization from a mixture of CH_2Cl_2/*n*-heptane; 214 mg; yield 78%; mp 159−160 °C (lit.[32] 166.1−166.9 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.04 (s, 6H), 6.74 (d, 2H, J = 8 Hz), 7.18 (d, 1H, J = 16 Hz), 7.56 (d, 2H, J = 8 Hz), 7.67−7.63 (m, 1H), 7.74−7.71 (m, 1H), 7.81(d, 1H, J = 16 Hz), 8.04−8.01 (m, 2H), 9.01 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 151.6 (C), 151.1 (C), 144.6 (CH), 144.5 (CH), 142.6 (C), 141.1 (C), 136.9 (CH), 130.1 (CH), 129.0 (CH), 128.9 (CH), 128.5 (CH), 124.1 (C), 120.6 (CH), 112.1 (CH), 40.3 (CH_3); HRMS (ESI$^+$, TOF) m/z calculated for $C_{18}H_{18}N_3$ (MH^+), 276.1501; found, 276.1499.

*2-[2-(4-Piperidin-1-yl-phenyl)-vinyl]-quinoxaline (**4e**):* Orange solid; purified by column chromatography (SiO_2, petroleum ether/EtAcO, 5:5) and crystallization from a mixture of CH_2Cl_2/*n*-heptane;

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132 mg; yield 42%; mp 143−144 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.64−1.60 (m, 2H), 1.71−1.70 (m, 4H), 3.30−3.28 (m, 4H), 6.93 (d, 2H, J = 8 Hz), 7.20 (d, 1H, J = 16 Hz), 7.55 (d, 2H, J = 8 Hz), 7.68−7.65 (m, 1H), 7.75−7.71 (m, 1H), 7.80 (d, 1H, J = 16 Hz), 8.05−8.02 (m, 2H), 9.01 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 152.5 (C), 151.5 (C), 144.6 (CH), 142.6 (C), 141.2 (C), 136.6 (CH), 130.2 (CH), 129.1 (CH), 129.0 (CH), 128.9 (CH),128.7 (CH), 126.0 (C), 121.5 (CH), 115.3 (CH), 49.5 (CH_2), 25.6 (CH_2), 24.4 (CH_2). Anal. Calcd for $C_{21}H_{21}N_3$: C, 79.97; H, 6.71; N, 13.32. Found: C, 80.19; H, 6.67; N, 13.12.

*2-[2-(4-N,N-Diphenylamino-phenyl)-vinyl]-quinoxaline (**4f**):* Yellow solid; purified by column chromatography (SiO_2, CH_2Cl_2); 180 mg; yield 45%; mp 115−116 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11−7.07 (m, 4H), 7.15 (dd, 4H, J_1 = 8.5 Hz, J_2 = 1.5 Hz), 7.27 (d, 1H, J = 16 Hz), 7.30 (dd, 4H, J_1 = 8 Hz, J_2 = 8.5 Hz), 7.52 (d, 2H, J = 8 Hz), 7.70−7.67 (m, 1H), 7.76−7.73 (m, 1H), 7.81 (d, 1H, J = 16 Hz), 8.05−8.03 (m, 2H), 9.02 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 151.1 (C), 149.0 (C), 147.2 (C), 144.5 (CH), 142.6 (C), 141.4 (C), 136.0 (CH), 130.3 (CH), 129.5 (CH), 129.2 (CH), 129.1 (CH), 129.0 (CH), 128.5 (CH), 125.2 (CH), 123.7 (CH), 123.1 (CH), 122.4 (CH). Anal. Calcd for $C_{28}H_{21}N_3$: C, 84.18; H, 5.30; N, 10.52. Found: C, 84.50; H, 5.26; N, 10.23.

*2-(Ferrocenyl-vinyl)-quinoxaline (**4g**):* Red solid; purified by crystallization from a mixture of CH_2Cl_2/*n*-heptane; 153 mg; yield 45%; mp 137−138 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.19 (s, 5H), 4.42 (s, 2H), 4.62 (s, 2H), 6.97 (d, 1H, J = 16 Hz), 7.73−7.67 (m, 2H), 7.72 (d, 1H, J = 16 Hz), 8.08−8.05 (m, 2H), 8.97 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 151.0 (C), 144.1 (CH), 142.6 (C), 141.2 (C), 136.7 (CH), 130.2 (CH), 129.2 (CH), 128.9 (CH), 128.7 (CH), 122.8 (CH), 82.2 (C), 70.4 (CH), 69.6 (CH), 68.0 (CH). Anal. Calcd for $C_{20}H_{16}FeN_2$: C, 70.61; H, 4.74; N, 8.23. Found: C, 70.37; H, 4.69; N, 8.00.

General Procedure for the Synthesis of 2-Arylvinylpyrazines and 3-Arylvinylpyridazines. A stirred mixture of methyldiazine (282 mg, 3 mmol) and KBu^{t}O (448 mg, 4 mmol) and the corresponding aldehyde (2 mmol) in refluxing THF (20 mL) was heated under reflux for 2 h under nitrogen. The mixture was allowed to cool, water was added, and the THF was evaporated under vacuum. The mixture was then extracted with EtAcO (3 × 25 mL) and dried ($MgSO_4$) and the solvent evaporated.

*2-[2-(4-N,N-Dimethylamino-phenyl)-vinyl]-pyrazine (**6a**):* Yellow solid; purified by column chromatography (SiO_2, EtOAc/petroleum ether, 3:7); 117 mg; yield 26%; mp 117−118 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.03 (s, 6H), 6.72 (d, 2H, J = 8 Hz), 6.94 (d, 1H, J = 16 Hz), 7.49 (d, 2H, J = 8 Hz), 7.67 (d, 1H, J = 16 Hz), 8.31 (d, 1H, J = 3 Hz), 8.48 (dd, 1H, J_1 = 3 Hz, J_2 = 2 Hz), 8.58 (d, 1H, J = 2 Hz); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 152.3 (C), 151.0 (C), 144.2 (CH), 143.4 (CH), 141.6 (CH), 135.5 (CH), 128.7 (CH), 124.2 (C), 119.3 (CH), 112.2 (CH), 40.3 (CH_3). Anal. Calcd for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.87; H, 6.67; N, 18.86.

*2-[2-(4-N,N-Diphenylamino-phenyl)-vinyl]-pyrazine (**6b**):* Yellow solid; purified by column chromatography (SiO_2, EtOAc/petroleum ether, 3:7); 237 mg; yield 34%; mp 135−136 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (d, 1H, J = 16 Hz), 7.09−7.05 (m, 4H), 7.14 (dd, 4H, J_1 = 8.5 Hz, J_2 = 1 Hz), 7.30−7.27 (m, 4H), 7.45 (d, 2H, J = 8 Hz), 7.68 (d, 1H, J = 16 Hz), 8.36 (d, 1H, J = 3 Hz), 8.51 (dd, 1H, J_1 = 3 Hz, J_2 = 2 Hz), 8.61 (d, 1H, J = 2 Hz); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 151.7 (C), 148.7 (C), 147.2 (C), 144.3 (CH), 143.6 (CH), 142.25 (CH), 134.7 (CH), 129.6 (C), 129.4 (CH), 128.3 (CH), 125.0 (CH), 123.6 (CH), 122.6 (CH), 121.9 (CH). Anal. Calcd for $C_{24}H_{19}N_3$: C, 82.49; H, 5.48; N, 12.03. Found: C, 82.28; H, 5.67; N, 11.81.

*3-[2-(4-N,N-Dimethylamino-phenyl)-vinyl]-pyridazine (**8**):* Orange solid; purified by column chromatography (SiO_2, EtOAc); 220 mg; yield 49%; mp 159−160 °C (lit.[33] 162 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.02 (s, 6H), 6.72 (d, 2H, J = 8 Hz), 7.15 (d, 1H, J = 16 Hz), 7.37 (dd, 1H, J_1 = 8 Hz, J_2 = 5 Hz), 7.50 (d, 2H, J = 8 Hz), 7.57 (dd, 1H, J_1 = 8 Hz, J_2 = 2 Hz), 7.60 (d, 1H, J = 16 Hz), 8.97 (dd, 1H, J_1 = 5 Hz, J_2 = 2 Hz); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 159.1 (C), 151.0 (C), 148.9 (CH), 135.4 (CH), 128.7 (CH), 126.2 (CH), 124.0 (C), 123.3 (CH), 120.3 (CH), 112.1 (CH), 40.3 (CH_3). Anal. Calcd for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.55; H, 6.73; N, 18.58.

General Procedure for Suzuki Cross-Coupling Reactions. A stirred mixture of bromo derivative (0.5 mmol), arylboronic acid (1 mmol), $Pd(PPh_3)_4$ (0.025 mmol), aqueous 1 M sodium carbonate (1 mmol, 1 mL), and ethanol (1 mL) in degassed toluene (10 mL) was heated under nitrogen for 15 h. The reaction mixture was cooled, filtered, and dissolved with a mixture of EtAcO and water 1:1 (50 mL) and the organic layer separated. The aqueous layer was extracted with EtAcO (2 × 25 mL). The combined organic extracts were dried with $MgSO_4$ and the solvents evaporated.

*4-[2-(4′-N,N-Dimethylamino-biphenyl-4-yl)-vinyl]-pyrimidine (**9a**):* Yellow solid; purified by recrystallization from $CHCl_3$; 114 mg; yield 76%; mp > 250 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.01 (s, 6H), 6.81 (d, 2H, J = 8 Hz), 7.06 (d, 1H, J = 16 Hz), 7.31 (d, 1H, J = 5 Hz), 7.55 (d, 2H, J = 8 Hz), 7.61 (d, 2H, J = 8 Hz), 7.62 (d, 2H, J = 8 Hz), 7.91 (d, 1H, J = 16 Hz), 8.66 (d, 1H, J = 5 Hz), 9.16 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 162.5 (C), 158.9 (CH), 157.3 (CH), 150.3 (C), 142.4 (C), 137.4 (CH), 133.2 (C), 128.2 (CH), 128.0 (C), 127.6 (CH), 126.4 (CH), 124.6 (CH), 118.6 (CH), 112.7 (CH). Anal. Calcd for $C_{20}H_{19}N_3$: C, 79.70; H, 6.35; N, 13.94. Found: C, 79.70; H, 6.36; N, 14.02.

*4-[2-(4′-N,N-Diphenylamino-biphenyl-4-yl)-vinyl]-pyrimidine (**9b**):* Yellow solid; purified by crystallization from a mixture of CH_2Cl_2/*n*-heptane; 187 mg; yield 88%; mp 125−126 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, 1H, J = 16 Hz), 7.06 (d, 2H, J = 8 Hz), 7.11 (t, 2H, J = 7 Hz), 7.14 (d, 4H, J = 7.5 Hz), 7.29−7.26 (m, 4H), 7.32 (d, 1H, J = 5 Hz), 7.50 (d, 2H, J = 8 Hz), 7.62 (d, 2H, J = 8 Hz), 7.65 (d, 2H, J = 8 Hz), 7.92 (d, 1H, J = 16 Hz), 8.67 (d, 1H, J = 5 Hz), 9.17 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 162.3 (C), 158.9 (CH), 157.4 (CH), 147.7 (C), 147.5 (C), 141.7 (C), 137.2 (CH), 134.0 (C), 133.8 (C), 129.4 (CH), 128.2 (CH), 127.6 (CH), 126.9 (C), 125.1 (CH), 124.6 (CH), 123.6 (CH), 123.2 (CH), 118.7 (CH). Anal. Calcd for $C_{30}H_{23}N_3$: C, 84.68; H, 5.45; N, 9.87. Found: C, 84.86; H, 5.79; N, 9.51.

*4-[2-(4′-N,N-Methoxy-biphenyl-4-yl)-vinyl]-pyrimidine (**9c**):* Beige solid; purified by recrystallization from $CHCl_3$/*n*-heptane; 84 mg; yield 58%; mp 215−216 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.99 (d, 2H, J = 8 Hz), 7.08 (d, 1H, J = 16 Hz), 7.32 (d, 1H, J = 5 Hz), 7.57 (d, 2H, J = 8 Hz), 7.60 (d, 2H, J = 8 Hz), 7.65 (d, 2H, J = 8 Hz), 7.92 (d, 1H, J = 16 Hz), 8.68 (s br, 1H), 9.17 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 162.3 (C), 159.6 (C), 158.9 (CH), 157.4 (CH), 141.9 (C), 137.2 (CH), 133.9 (C), 132.8 (C), 128.2 (CH), 128.1 (CH), 127.1 (CH), 125.1 (CH), 118.7 (CH), 114.4 (CH). Anal. Calcd for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25; N, 9.65. Found: C, 78.63; H, 6.16; N, 9.49.

*2-[2-(4′-N,N-Dimethylamino-biphenyl-4-yl)-vinyl]-quinoxaline (**10a**):* Orange solid; purified by crystallization from a mixture of $CHCl_3$/*n*-heptane; 105 mg; yield 60%; mp 208−209 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.02 (s, 6H), 6.82 (d, 2H, J = 8 Hz), 7.40 (d, 1H, J = 16 Hz), 7.57 (d, 2H, J = 8 Hz), 7.64 (d, 2H, J = 8 Hz), 7.72−7.69 (m, 3H), 7.78−7.75 (m, 1H), 7.91 (d, 1H, J = 16 Hz), 8.08−8.05 (m, 2H), 9.06 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 150.9 (C), 150.2 (C), 144.5 (CH), 142.5 (C), 142.1 (C), 141.5 (C), 136.3 (CH), 133.6 (C), 130.3 (CH), 129.2 (CH), 129.1 (CH), 128.1 (C), 128.0 (2 × CH), 127.6 (CH), 126.5 (CH), 124.4 (CH), 112.7 (CH), 40.5 (CH_3); HRMS (ESI$^+$, TOF) m/z calculated for $C_{24}H_{22}N_3$ (MH^+), 352.1814; found, 352.1814.

*2-[2-(4′-N,N-Diphenylamino-biphenyl-4-yl)-vinyl]-quinoxaline (**10b**):* Yellow solid; purified by crystallization from a mixture of $CHCl_3$/*n*-heptane; 214 mg; yield 90%; mp 131−132 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7−11−7.07 (m, 4H), 7.15 (dd, 4H, J_1 = 8.5 Hz, J_2 = 1.5 Hz), 7.27 (d, 1H, J = 16 Hz), 7.30 (dd, 4H, J_1 = 8 Hz, J_2 = 8.5 Hz), 7.52 (d, 2H, J = 8 Hz), 7.57 (d, 2H, J = 8 Hz), 7.64 (d, 2H, J = 8 Hz), 7.70−7.67 (m, 1H), 7.76−7.73 (m, 1H), 7.91 (d, 1H, J = 16 Hz), 8.08−8.07 (m, 2H), 9.06 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 150.8 (C), 147.64 (C), 147.56 (C), 144.5 (CH), 142.5 (C), 141.6 (C), 141.5 (C), 136.1 (CH), 134.5 (C), 133.9 (C), 132.2 (CH), 123.1 (CH), 129.4 (CH), 129.2 (CH), 128.6 (CH), 128.5 (CH),

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128.0 (CH), 127.6 (CH), 126.9 (CH), 124.6 (CH), 123.7 (CH), 123.2 (CH). Anal. Calcd for $C_{34}H_{25}N_3$: C, 85.87; H, 5.30; N, 8.84. Found: C, 86.25; H, 4.99; N, 8.65.

2-[2-(4′-N,N-Methoxy-biphenyl-4-yl)-vinyl]-quinoxaline ***(10c):*** Beige solid; purified by crystallization from a mixture of $CHCl_3$/*n*-heptane; 152 mg; yield 90%; mp 148−149 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.87 (s, 3H), 7.01 (d, 2H, J = 8 Hz), 7.42 (d, 1H, J = 16 Hz), 7.59 (d, 2H, J = 8 Hz), 7.64 (d, 2H, J = 8 Hz), 7.79−7.70 (m, 4H), 7.92 (d, 1H, J = 16 Hz), 8.08 (d, 2H, J = 8 Hz), 9.07 (s, 1H); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 159.5 (C), 150.7 (C), 144.5 (CH), 142.5 (C), 141.63 (C), 141.58 (C), 136.1 (CH), 134.4 (C), 132.8 (CH), 130.3 (CH), 129.25 (CH), 129.19 (CH), 129.17 (CH), 128.1 (CH), 128.0 (CH), 127.1 (CH), 124.9 (CH), 114.4 (CH), 55.4 (CH_3); HRMS (ESI$^+$, TOF) m/z calculated for $C_{23}H_{19}N_2O$ (MH^+), 339.1497; found, 339.1496.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H NMR and ^{13}C NMR spectra for all compounds and plots of emission maxima versus $\Delta E_T(30)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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