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Donor-Linker-Acceptor (D-π-A) diazine chromophores with extended π-conjugated core: synthesis, photophysical and second order nonlinear optical properties.

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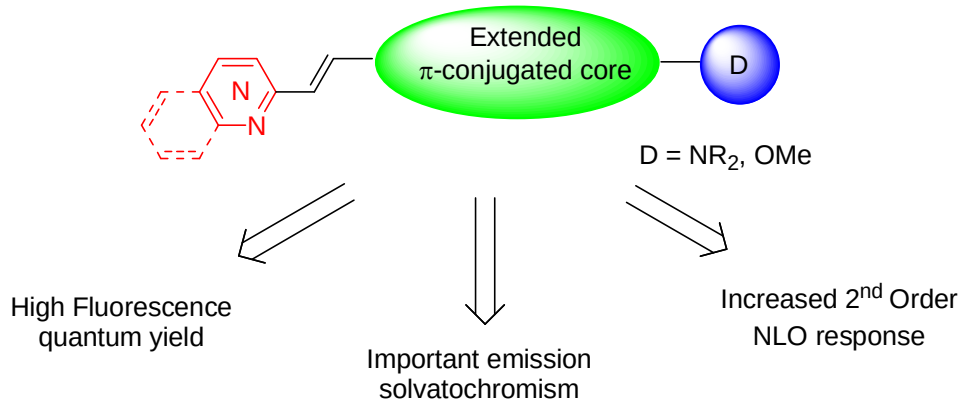
Synopsis TOC



The synthesis and photophysical properties of a series of push-pull pyrimidine and quinoxaline chromophores with an extended π-conjugated core are reported.

Abstract

The synthesis of a series of push-pull pyrimidine and quinoxaline chromophores with an extended π-conjugated core is reported. Starting from a bromoarylvinyldiazine derivative, the key step in the preparation of the chromophores consists of a Sonogashira cross-coupling reaction. The photophysical properties of the compounds are described. A strong positive emission solvatochromism, typical for dyes presenting Intramolecular Charge Transfer (ICT), is observed, in particular for amino substituted derivatives with larger solvatochromic range than known analogous chromophores with smaller π-conjugated core. The second order non linear optical (NLO) properties were investigated for some of the compounds and a comparison with the NLO responses of already described diazine chromophores exhibits a significant enhancement of the NLO properties by extension of the π-conjugated core.

Key words: Pyrimidine ; Quinoxaline ; Push-Pull ; Non-linear Optics ; Fluorescence

Introduction

During the past decades, push-pull structures composed of a π-conjugated core substituted by electron-donating (D) and electron-attracting (A) groups were extensively studied in materials chemistry.[1] Indeed ICT in such D-π-A structure leads to polarization of the chromophore and generation of molecular dipole.[2] Push-pull molecules have found applications as sensitizers for dye sensitized solar-cells (DSSCs),[3] emitters for organic light emitting diodes (OLEDs)[4] and various fluorescent sensors.[5] D-π-A is also the typical structure of second-order NLO chromophores[6] with applications in green lasers obtained from infrared sources through frequency doubling, second harmonic generation microscopy or in terahertz wave generation.[7]

Diazines consist of 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),[8] pyrimidine (1,3-diazine),[9] and pyrazine (1,4-diazine).[10] The (benzo)diazines with their highly π–deficient aromatic character are good candidates to be incorporated as electron-withdrawing groups into push-pull scaffolds favoring ICT. The use of diazine rings in the structure of π–conjugated materials has been recently reviewed.[11] During the past decade, we have described a large library of (benzo)diazine chromophores with fluorescent sensing applications and NLO properties.[12] In the literature, there are only few examples of diazine chromophores with second-order NLO properties.[13] Among them we have described a series of 4-arylvinylpyrimidine and 2-arylvinylquinoxaline derivatives that exhibit moderate second-order NLO responses.[14]

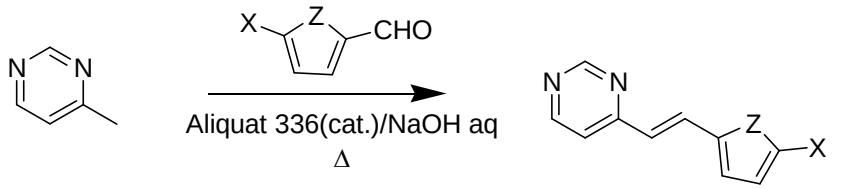
Photophysical properties of push-pull molecules can be easily tuned by varying various parameters.[15] In particular, two design strategies were described for increasing their second-order NLO polarizability.[16] The first one consists in increasing the strength of the donor and /or the acceptor. Recently, we have described the *N*-methylation and the complexation of pyrimidine push-pull chromophores resulting in a dramatic increase of the second-order NLO response.[17] The second strategy consists in the elongation of the conjugation pathway.

In this context, the aim of the present article is to describe the synthesis of seventeen new diazine chromophores with extended π-conjugated core. Indeed, we thought that it would be of interest to study the influence of the nature of the π-conjugated linker on the linear and second-order NLO properties on diazine push-pull chromophores.

Results and discussion.

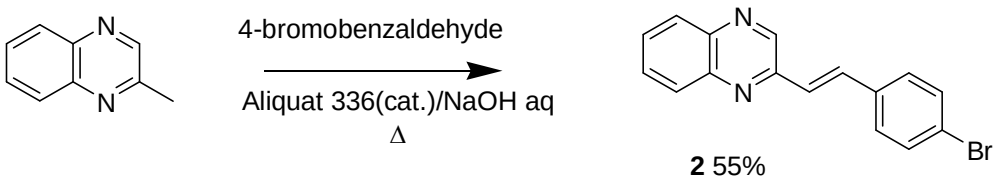
Preparation of chromophores. Halogenated **s**tarting materials were obtained by condensation of 4-methylpyrimidine or 2-methylquinoxaline with the corresponding aromatic

aldehydes in boiling aqueous 5M NaOH using aliquat 336 as a phase-transfer catalyst according to the conditions initially described by Vanden Eynde (Schemes 1-2).[18] As previously observed, this synthetic protocol led to the selective formation of *E*-configured vinylene bridges,[12a,b,f,14,19] compounds **1a-c** and **2** where obtained with moderate to good yield.



1a Z = C=C, X = Br 78%
1b Z = C=C, X = I 84%
1c Z = S, X = Br 79%

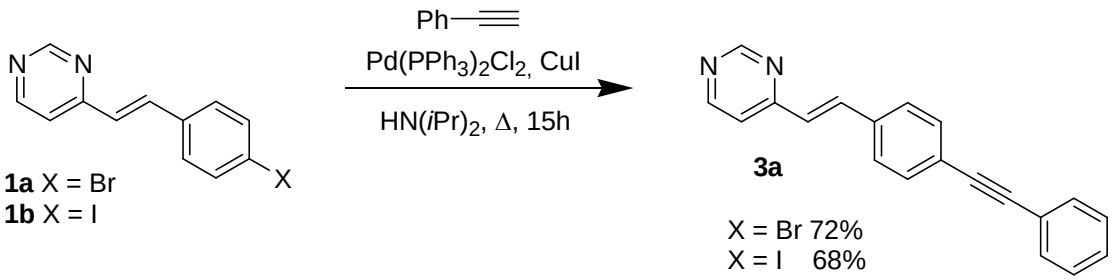
Scheme 1 : Synthesis of compounds 1a-c



2 55%

Scheme 2 : Synthesis of compound 2

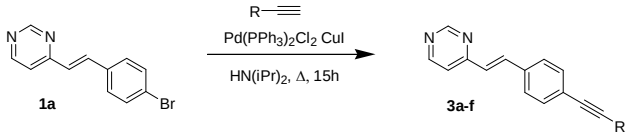
In order to compare the reactivity of bromo (**1a**) and iodo (**1b**) derivatives in Sonogashira cross-coupling reaction, the two compounds were tested with phenylacetylene using diisopropylamine as solvent in a pressure tube at 80°C, according to the conditions initially described on chloropyrimidines (Scheme 3).[20] In these conditions, compound **3a** was obtained with similar yield when starting from **1a** or **1b**. It should be noted that compound **3a** can be also obtained at room temperature in a mixture of triethylamine and THF starting from iodo compound **1b** with a correct yield (64%), which is not possible with bromo compound **1a**. Nevertheless, due to the high cost of 4-iodobenzaldehyde, we decided to start from bromo derivatives for all the following reactions.

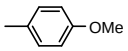
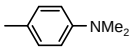
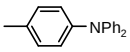


Scheme 3: Synthesis of compounds 3a

Similar conditions were used to obtain compounds **3**, **4** and **5** starting from bromo derivatives **1a**, **1c** and **2** respectively and a variety of alkynes (Tables 1-3). In case of compounds **3e**, **4e** and **5e**, the trimethylsilyl group can be cleaved with potassiun hydroxide in methanol to obtain the corresponding terminal alkynes **3f**, **4f** and **5f**. These compounds appear as interesting building blocks for the synthesis of more complex structures.

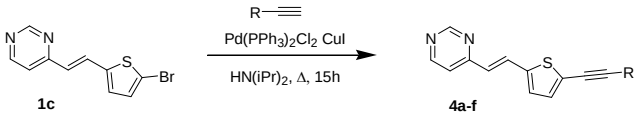
Table 1: Sonogashira Cross-coupling reaction with compound 1a

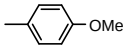


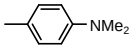
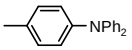
Compd	R	Isolated yield (%)
3a		72
3b		56
3c		59
3d		81
3e	$SiMe_3$	57
3f[a]	H	83

[a] : obtained by deprotection of compound **3e** (KOH/MeOH rt, 15 min)

Table 2: Sonogashira Cross-coupling reaction with compound 1c

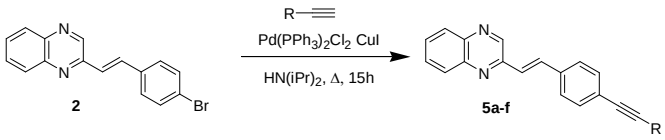


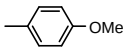
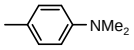
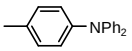
Compd	R	Isolated yield (%)
4a		69
4b		54

4c		79
4d		89
4e	$SiMe_3$	Non isolated
4f[a]	H	56[b]

[a] : obtained by deprotection of compound **4e** (KOH/MeOH rt, 15 min) [b]: over two steps

Table 3: Sonogashira Cross-coupling reaction with compound 2



Compd	R	Isolated yield (%)
5a		95
5b		83
5c		68
5d		72
5e	$SiMe_3$	75
5f[a]	H	84

[a] : obtained by deprotection of compound **5e** (KOH/MeOH rt, 15 min)

All new compounds are readily soluble in THF, chloroform and dichloromethane and were characterized using a variety of analytical techniques (^1H and ^{13}C NMR, high-resolution mass spectrometry, UV-visible and fluorescence spectrometry). NMR experiments proved very useful to confirm the structures of the compounds (see Experimental Section and Supporting Information). The selectivity of the Knoevenagel reactions was sufficiently high to generate all-*E* 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 *E-Z* isomerization when allowed to stand in $CDCl_3$ solution under sunlight at room temperature for several days as observed by NMR.

UV/Vis and PL Spectroscopy. The UV-Vis and photoluminescence (PL) spectroscopic data of various oligomers measured in dichloromethane and in toluene at 25°C are presented in tables 4 and S40. 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 **3c**, **4d** and **5b** in dichloromethane are shown in Figure 1. Under these conditions, self-absorption effects were not observed. All compounds are photostable and did not undergo *E-Z* isomerization under the analysis conditions.

In dichloromethane, all compounds show absorption wavelengths (λ_{max}) in the UV or visible region (347-419 nm). In some cases, a second or even a third absorption band of higher energy attributed to π-π^* transition can be observed. All compounds are luminescent with, in some cases, high quantum yield (up to 0.8). Very large Stokes shifts, in some case superior to 9000 cm^{-1} were observed, indicating large differences (vibrational, electronic, geometric) between the Franck-Condon state and the excited state.

For the three series of compounds an important substituent effect is observed. For instance for compounds **3**, non-substituted compound **3a** exhibits an emission maxima in CH_2Cl_2 at 420 nm this maxima is shifted to 612 nm in case of dimethylamino substituted compound **3c**. Compounds **3** and **5** are red-shifted in absorption and emission when compared with corresponding 4-arylvinylpyrimidines and 2-arylvinylquinoxalines.[14,21] Whereas 4-(phenylvinyl)pyrimidine and 4-(*p*-methoxyphenylvinyl)pyrimidine are slighltly fluorescent, extention of the conjugation leads to a dramatic increase of the fluorescence quantum yield. It should be noted however that in the case of quinoxaline derivatives **5c-d** the extension of the π-conjugated core leads to a diminution of the fluorescence quantum yield in dichloromethane, nevertheless these values are much higher in toluene. Comparison of compounds **3b-d** with corresponding bisphenylenevinylene pyrimidine indicates that the

introduction of a triple bond between the two phenyl rings also leads to red-shifted spectra. This tendency is less significant with quinoxaline derivatives.

Comparison of quinoxaline derivatives **5** with pyrimidine derivatives **3** showed a bathochromic shift of absorption and emission spectra in case of quinoxaline derivatives. Concerning pyrimidine derivatives, when the π-conjugated core includes a thienyl ring (compounds **4**) instead of a phenyl ring (compounds **3**), a red shift in absorption and emission is clearly observed in toluene. This tendency is not observed in dichloromethane for the most electron-donating amino groups.

Table 4. UV/Vis and photoluminescence (PL) data in CH_2Cl_2

Compd[a]	UV/vis λ_{max}, nm (ε,$mM^{-1}\cdot cm^{-1}$)	PL λ_{max}, nm	Φ_F[b]	Stokes shift cm^{-1}
3a	347 (33.0)	420	0.11	5009
3b	355 (28.5)	460	0.51	6429
3c	312 (18.8), 391 (25.0)	612	0.54	9236
3d	314 (32.9), 394 (34.4)	590	0.41	8432
4a	278 (10.1), 383 (34.1)	462	<0.01	4465
4b	383 (36.1)	489	0.04	5660
4c	328 (16.7), 419 (31.5)	607	0.80	7392
4d	305sh (22.3), 342 (26,4), 416 (43.3)	583	0.79	6886
5a	308 (22.9), 381 (38.1)	447	0.39	3875
5b	302 (17.3), 383 (30.6)	480	0.77	5276
5c	321 (26.1), 406 (33.7)	647	0.07	9174
5d	306 (27.2), 333 (27.5), 403 (35.7)	630	0.37	8941

[a] All spectra were recorded at room temperature at $c = 1.0 \times 10^{-5}$ M to 3.0×10^{-5} M for absorption and $c = 1.0 \times 10^{-6}$ M to 3.0×10^{-6} M for emission. [b] Fluorescence quantum yield (±10%) determined relative to 9,10-Bis-phenylethynyl-anthracene in cyclohexane ($\Phi_F = 1.00$).[22]

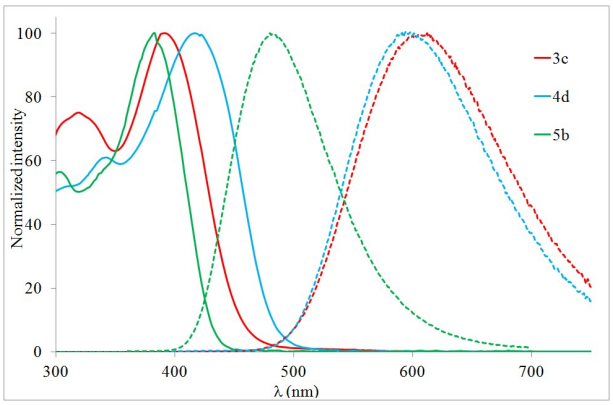


Figure 1: Normalized UV/Vis (solid line) and emission spectra (brocken line) of compounds 3c, 4d and 5b.

In an effort to gain further insight into the photophysical process within these push-pull molecules, we investigated their emission behavior in different aprotic solvents. The results of these investigations are summarized in table 5. For all compounds, a bathochromic shift of the emission band is observed with increasing solvent polarity as predicted by the Dimroth–Reichardt polarity parameter ($E_T(30)$).[23] 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.[24] It should be noted that in low polar solvents (hexane and sometimes toluene) two well developed emission bands are observed, which may be due to the partial aggregation of the chromophores. As an example the PL spectra for compound **4d** and color change under UV irradiation for compound **4c** are shown in figures 2-3.

Table 5. Emission solvatochromism of diazines chromophores in various aprotic solvents

Compd	Hexane $E_T(30)^a$ = 30.9 λ_{max}, nm	Toluene $E_T(30)^a$ = 33.9 λ_{max}, nm	THF $E_T(30)^a$ = 37.4 λ_{max}, nm	CH_2Cl_2 $\Delta E_T(30)^a$ = 40.7 λ_{max}, nm	Acetone $\Delta E_T(30)^a$ = 42.2 λ_{max}, nm	MeCN $\Delta E_T(30)^a$ = 45.6 λ_{max}, nm	DMSO $\Delta E_T(30)^a$ = 45.1 λ_{max}, nm
3a	376, 398	390, 407	407	420	421	422	423
3b	393, 412	414, 427	445	460	474	485	493
3c	459	501	590	612	659	-[b]	-[b]
3d	434, 451	476	554	590	620	653	[illegible]
4a	417, 440	448	453	462	455	465	475
4b	427, 451	459	479	489	490	497	507
4c	496	526	600	607	650	679	[illegible]
4d	468, 491	496	557	583	621	649	656
5a	414, 436	426	430	447	446	448	453
5b	425	440	459	480	484	508	511
5c	464	518	634	647	-[b]	-[b]	-[b]
5d	458	490	584	630	671	-[b]	-[b]

[a] Dimroth–Reichardt polarity parameter,kJ·mol^{-1}. [b] no signal detected

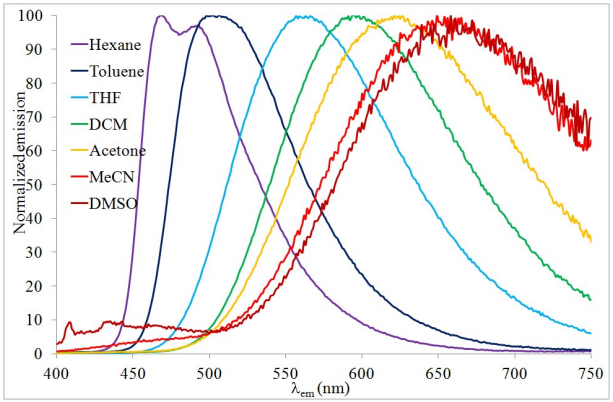


Figure 2: Normalized emission of compound 4d in various solvents

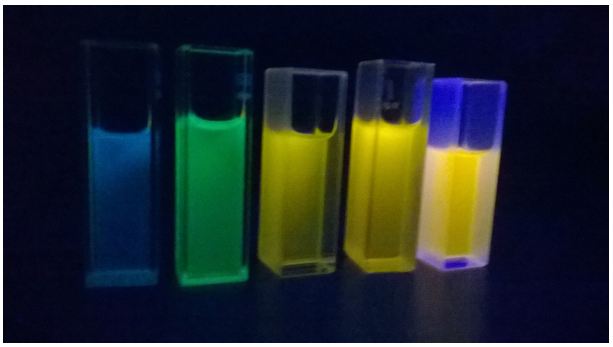


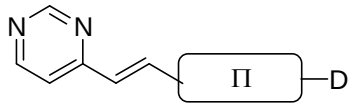
Figure 3: Color of solution of 4c in various solvents (Hexane, Toluene, $CHCl_3$, THF, CH_2Cl_2) (c = 10^{-5} M).

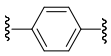
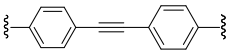
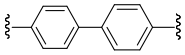
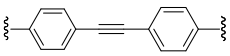
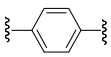
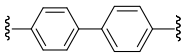
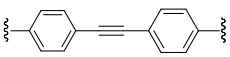
All the amino substituted derivatives exhibit extended solvatochromic range. The highest range between hexane and dichloromethane is observed for compound **5c** ($\Delta\lambda$ = 183 nm, $\Delta\nu$

= 6095 cm^{-1}). It should be noted however that the red-shift observed, when the polarity is increased, is associated with a dramatic decrease of the fluorescence intensity. As shown in tables 6 and S41, extension of the π-conjugated core leads to a dramatic increase of the solvatochromic range.

For all of the compounds, the emission maxima were plotted versus $E_T(30)$ (see supporting information S42-S43). A good linearity was obtained for all the compounds. The slopes of the corresponding regression lines (SP) are good indications of the intensity of the ICT into the chromophores. When comparing the SP values for pyrimidine derivatives **3** and quinoxaline derivatives **5**, a more intense solvatochromism is observed for the quinoxaline derivatives **5**. When comparing compounds **3** and **4**, replacing a 1,4-phenylene linker by a 2,5-thienylene one decreases the intensity of the solvatochromism.

Table 6: Solvatochromic range between hexane/heptane and dichloromethane for compounds 3b-d and their analogues



Compd	D	Π	Δλ (nm)	Δν(cm^{-1})
	OMe		34[a]	2118[a]
3b	**OMe**		48	2533
	NMe_2		116[a]	4500[a]
3c	**NMe_2**		153	5447
	NPh_2		83[b]	3562[b]
	NPh_2		104[b]	4710[b]
3d	**NPh_2**		139	5224

[a] : data from ref 20 [b] : data from ref 13

Second Order Non Linear Optical Properties.

Nonlinearities of the selected dyes **3c,d**, **4b-d** and **5c,d** were evaluated by measuring the $\mu\beta$ coefficients by means of the Electric Field Induced Second Harmonic Generation (EFISH) technique, at 1907 nm fundamental wavelength. The obtained values are reported in Table 7 and can be considered not affected by resonance effects, being the second harmonic signal generated from chloroform solutions of these dyes (953.5 nm) far beyond the range of linear absorption, as it can be evinced from UV-Visible spectra.

Table 7. $\mu\beta$ values for compounds 3c,d, 4b-d, and 5c,d.

	3c	**3d**	**4b**	**4c**	**4d**	**5c**	**5d**
$\mu\beta$ [10^{-48} esu][a]	560	280	150	440	400	280	200

[a]: $\mu\beta$ (2ω) at 1900 nm in $CHCl_3$. Molecular concentrations used for the measurements were in the range 10^{-3} to 10^{-2} M. μβ ± 10%.

All the $\mu\beta$ values, reported in table 7 are positive and range from 150 to 560 × 10^{-48} esu. These values which are lower or similar to the common benchmark of organic NLO chromophores Disperse Red 1, indicate the occurrence of more polarized Frank-Condon excited states than the ground states. As exemplified in table 7, the $\mu\beta$ values are slightly influenced by structural or electronic changes. The pyrimidine derivative **4b** gave the lower NLO response, as expected from the modest donor strength of the methoxy group. For more polarized compounds bearing an amino donor group, it appears that the pyrimidine derivatives **3** exhibits higher $\mu\beta$ values than the quinoxaline derivatives **5**. The $\mu\beta$ value difference is more pronounced for the dimethylamino derivatives (**3c**, **5c**). A similar tendency for pyrimidine or quinoxaline push-pull dimethylaminophenylvinyl chromophores has been observed previously.[14] Except for compounds **4c** and **4d** which gave quasi-similar $\mu\beta$ values, dimethylamino derivatives are better NLO chromophores than their diphenylamino analogues.

These results are in agreement with the better donor capacity of the dimethylamino group.[17] Concerning the replacement of a 1,4-phenylene ring by a 2,5-thienylene unit in the spacer, two opposite variations are observed: an increase of $\mu\beta$ for the diphenylamino derivatives **3d**, **4d** ($\mu\beta_{4d}/\mu\beta_{3d}$ =1.43) and a decrease of $\mu\beta$ for the dimethylamino derivatives **3c**, **4c** ($\mu\beta_{4c}/\mu\beta_{3c}$ =0.78). This result does not agree with the bathochromic shift observed upon thienyl substitution for the ICT band. For similar dialkylamino and diphenylamino push-pull compounds bearing various acceptor groups, it has been shown that substitution of a 1,4-phenylene linker for a 2,5-thienylene bridge slightly (for modest acceptors) or widely (for stronger acceptors) increases the $\mu\beta$ values.[25] This is due to the lower resonance energy of the thiophene ring which allows a better charge redistribution than the benzene ring.[26] For the dimethylamino compounds **3c** and **4c**, the decrease of $\mu\beta$ upon phenyl-thienyl change may be explained in terms of relation between β and the extent of ground-state polarization in the molecule.[25d] Other experimental and theoretical investigations would be necessary to clarify this point.

Finally, comparison with analogous derivatives with phenylenevinylene or biphenylenevinylene π-conjugated core[14,17] indicates that the extension of the π-conjugated linker increases the $\mu\beta$ value of pyrimidine derivatives. Inclusion of a carbon-carbon triple bond between the two phenyl rings in 4-(*p*-dimethylaminobiphenylvinyl)pyrimidine chromophore (compound **3c**) is, however, less effective in term of $\mu\beta$ enhancement than adding a phenyl ring in 4-(*p*-dimethylaminophenylvinyl)pyrimidine.[14] It should be noted that the influence of the π-conjugated linker is lower than the influence of methylation or complexation of the diazine electron-attracting group or of electron-donating part. Interestingly, the NLO response is not proportional to the solvatochromic range described above.

Conclusions

In conclusion, we have successfully synthesized ad characterized a series of push-pull diazines derivatives with extended π-conjugated core. These compounds exhibit absorption maxima in the UV or visible region and are highly fluorescent. For amino substituted derivatives, 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 amino electron-donating groups are present in the molecule. The solvatochromic ranges observed are larger than for analogue structures with smaller π-conjugated core. Extension of the π-conjugated linker results also in a moderate increase of the 2nd order NLO response.

Experimental Section

General. Compounds **1a** and **2** were synthesized according to reported procedure.[14] 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. Fluorescence spectra were corrected. 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. Experimental details for EFISH techniques are given elsewhere.[13g]

General procedure for the synthesis of 4-Arylvinylpyrimidines : A stirred mixture of 4-methylpyrimidine (470mg, 5 mmol) and the corresponding aldehyde (5 mmol) in aqueous sodium hydroxide (5 M, 20 mL) containing Aliquat 336 (215 mg, 0.5 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 recrystallization from *n*-heptane/CH_2Cl_2.

General procedure for Sonogashira Cross-coupling reactions : A suspension of bromo derivative (0.5 mmol), $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol), and CuI (5mg, 0.025 mmol) in diisopropylamine (5 mL) was degazed three times in a pressure tube. The acetylene derivative (0.6 mmol) was then added. The mixture was heated at 80°C overnight. The suspension was then diluted with a mixture of water and dichloromethane (1:1, 30 mL) and the organic layer was extracted with dichloromethane (2 × 30 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and evaporated.

General procedure for trimethylsilyl group deprotection: A mixture of trimethylsilylethynyl derivativ (1 mmol) and a solution of potassium hydroxyde in methanol (1M, 10 mL) was stirred at room temperature for 15 min. The solution was then neutralized with 1 M aqueous HCl and extracted with dichloromethane (3 x 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and evaporated.

4-[2-(4-Iodophenyl)-vinyl]-pyrimidine (1b): cream solid ; 1.29 g; yield 84%; mp : 173-175°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, 1H, *J* = 16 Hz, H_{vinyl}), 7.34 (d, 2H, *J* = 8 Hz, H_{Ph}), 7.38 (d, 1H, *J* = 5 Hz, $H5_{pyrim}$), 7.76 (d, 2H, *J* = 8 Hz, H_{Ph}), 7.91 (d, 1H, *J* = 16 Hz, H_{vinyl}), 8.72 (d, 1H, *J* = 5 Hz, $H6_{pyrim}$), 9.19 (s, 1H, $H2_{pyrim}$); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) δ 161.9 (C), 158.9 (CH), 157.6 (CH), 138.1 (CH), 136.3 (C), 135.0 (CH), 129.2 (CH), 126.2 (CH), 118.9 (CH), 95.5 (C). Anal. Calcd for $C_{12}H_9IN_2$: C, 46.78; H, 2.94; N, 9.09. Found C, 47.08; H, 2.91; N, 8.81.

4-[2-(5-Bromothiophen-2-yl)-vinyl]-pyrimidine (1c): pale yellow solid ; 1.06 g; yield 79%; mp: 116-118°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.73 (d, 1H, *J* = 16 Hz, H_{vinyl}), 7.01 (d, 1H, *J* = 3.9 Hz, H_{thio}), 7.01 (d, 1H, *J* = 3.9 Hz, H_{thio}), 7.23 (d, 1H, J_1 = 5.1 Hz, J_2 = 1.2 Hz, $H5_{pyrim}$),

7.93 (d, 1H, *J* = 16 Hz, H_{vinyl}), 8.67 (d, 1H, *J* = 5.1 Hz, $H6_{pyrim}$), 9.14 (s, 1H, $H2_{pyrim}$); ^{13}C NMR and JMOD (75 MHz, $CDCl_3$) δ 161.5 (C), 158.8 (CH), 157.5 (CH), 142.6 (C), 131.0 (CH), 129.9 (CH), 129.4 (CH), 124.8 (CH), 118.8 (CH), 114.7 (C); HRMS (ESI/ASAP) *m/z* calculated for $C_{10}H_8N_2{}^{79}BrS$ $[M+H]^+$: 266.9592, found 266.9590.

4-[2-(4-Phenylethynyl-phenyl)-vinyl]-pyrimidine (3a): Pale yellow solid; obtained according to general procedure and purified by column chromatography (SiO_2, Petroleum Ether/EtOAc 7/3); yield 72% (101 mg), mp: 190-192°C; ^1H NMR (500MHz, $CDCl_3$) *δ* 7.08 (d, 1H, *J* = 16.0 Hz, H_{vinyl}), 7.32 (dd, 1H, J_1 = 5.0 Hz, J_2 = 1.0 Hz, $H5_{pyrim}$), 7.37-7.35 (m, 3H, H_{Ph}), 7.60-7.54 (m, 6H, H_{Ph}), 7.89 (d, 1H, *J* = 16.0 Hz, H_{vinyl}), 8.69 (d, 1H, *J* = 5.0 Hz, $H6_{pyrim}$), 9.18 (s, 1H, $H2_{pyrim}$); ^{13}C NMR and JMOD (125 MHz, $CDCl_3$) *δ* 89.2 (C), 91.4 (C), 118.9 (CH), 123.1 (C), 124.4 (C), 126.2 (CH), 127.7 (CH), 128.4 (CH), 128.5 (CH), 131.7 (CH), 132.1 (CH), 135.4 (C), 136.7 (CH), 157.5 (CH), 159.0 (CH), 162.0 (C). HRMS (ESI/ASAP) *m/z* calculated for $C_{20}H_{15}N_2$ $[M+H]^+$: 283.1230, found 283.1227.

4-{2-[4-(4-Methoxyphenylethynyl)-phenyl]-vinyl}-pyrimidine (3b): Orange solid; obtained according to general procedure and purified by column chromatography (SiO_2, Petroleum Ether/EtOAc 1/1); yield 56% (87 mg), mp: 191-193°C; ^1H NMR (300MHz, $CDCl_3$) *δ* 3.86 (s, 3H, H_{OMe}), 6.91 (d, 2H, *J* =8.7 Hz, H_{Ph}), 7.08 (d, 1H, *J* = 15.9 Hz, H_{vinyl}), 7.33 (dd, 1H, J_1 = 5.0 Hz, J_2 = 1.0 Hz, $H5_{pyrim}$), 7.50 (d, 2H, *J* =8.7 Hz, H_{Ph}), 7.55 (d, 2H, *J* =8.7 Hz, H_{Ph}), 7.60 (d, 2H, *J* =8.7 Hz, H_{Ph}), 7.91 (d, 1H, *J* = 15.9 Hz, H_{vinyl}), 8.70 (d, 1H, *J* = 5.0 Hz, $H6_{pyrim}$), 9.20 (s, 1H, $H2_{pyrim}$); ^{13}C NMR and JMOD (75 MHz, $CDCl_3$) *δ* 55.3 (CH_3), 88.0 (C), 91.5 (C), 114.1 (CH), 115.2 (C), 118.8 (CH), 124.8 (C), 126.0 (CH), 127.6 (CH), 131.9 (CH), 133.2 (CH), 135.0 (C), 136.4 (CH), 157.5 (CH), 158.9 (CH), 159.9 (C), 162.1 (C). HRMS (ESI/ASAP) *m/z* calculated for $C_{21}H_{17}N_2O$ $[M+H]^+$: 313.1335, found 313.1338.

4-{2-[4-(4-*N*,*N*-dimethylaminophenylethynyl)-phenyl]-vinyl}-pyrimidine (3c): Orange solid; obtained according to general procedure and purified by column chromatography (SiO_2, Petroleum Ether/EtOAc 1/1); yield 59% (96 mg), mp: 261-263°C; ^{1}H NMR (300MHz, $CDCl_3$) δ 3.02 (s, 6H, H_{NMe2}), 6.68 (d, 2H, J =8.7 Hz, H_{Ph}), 7.06 (d, 1H, J = 15.9 Hz, H_{vinyl}), 7.33 (d, 1H, J = 5.0 Hz, H_{5pyrim}), 7.44 (d, 2H, J =8.7 Hz, H_{Ph}), 7.53 (d, 2H, J =8.7 Hz, H_{Ph}), 7.58 (d, 2H, J =8.7 Hz, H_{Ph}), 7.89 (d, 1H, J = 15.9 Hz, H_{vinyl}), 8.70 (d, 1H, J = 5.0 Hz, $H6_{pyrim}$), 9.18 (s, 1H, $H2_{pyrim}$); ^{13}C NMR and JMOD (75 MHz, $CDCl_3$) δ 40.1 (CH_3), 87.4 (C), 93.0 (C), 109.7 (C), 111.8 (C), 118.7 (CH), 125.5 (C), 125.6 (CH), 127.6 (CH), 131.7 (CH), 132.8 (CH), 134.5 (C), 136.9 (CH), 150.3 (C), 157.4 (CH), 158.9 (CH), 162.2 (C). HRMS (ESI/ASAP) *m/z* calculated for $C_{21}H_{17}N_2O$ $[M+H]^+$: 326.1652, found 326.1650.

4-{2-[4-(4-*N*,*N*-diphenylaminophenylethynyl)-phenyl]-vinyl}-pyrimidine (3d): Orange solid; obtained according to general procedure and purified by column chromatography (SiO_2, Petroleum Ether/EtOAc 7/3); yield 81% (181 mg), mp: 185-187°C; ^{1}H NMR (300MHz, $CDCl_3$) δ 7.13-7.00 (m, 9H, H_{Ph}+H_{vinyl}), 7.31-7.27 (m, 5H, H_{Ph}+$H5_{pyrim}$), 7.38 (d, 2H, J =8.7 Hz, H_{Ph}), 7.53 (d, 2H, J =8.7 Hz, H_{Ph}), 7.58 (d, 2H, J =8.7 Hz, H_{Ph}), 7.88 (d, 1H, J = 15.9 Hz, H_{vinyl}), 8.68 (d, 1H, J = 5.0 Hz, $H6_{pyrim}$), 9.17 (s, 1H, $H2_{pyrim}$); ^{13}C NMR and JMOD (75 MHz, $CDCl_3$) δ 88.6 (C), 91.9 (C), 115.7 (C), 118.8 (CH), 122.2 (CH), 123.7 (CH), 124.8 (C), 125.1 (CH), 126.0 (CH), 127.6 (CH), 129.4 (CH), 131.9 (CH), 132.6 (CH), 135.0 (C), 136.8 (CH), 147.2 (C), 148.2 (C), 157.5 (CH), 158.9 (CH), 162.1 (C). HRMS (ESI/ASAP) *m/z* calculated for $C_{32}H_{24}N_3$ $[M+H]^+$: 450.1970, found 450.1972.

4-[2-(4-Trimethylsilylethynyl-phenyl)-vinyl]-pyrimidine (3e): Beige solid; obtained according to general procedure and purified by column chromatography (SiO_2, Petroleum Ether/EtOAc 9/1 then EtOAc); yield 57% (79 mg), mp: 125-127°C; ^{1}H NMR (300MHz, $CDCl_3$) δ 0.25 (s, 9H, H_{SiMe3}), 7.00 (d, 1H, J = 15.9 Hz, H_{vinyl}), 7.25 (d, 1H, J = 5.0 Hz,

$H5_{pyrim}$), 7.45 (broad s, 4H, H_{Ph}) 7.82 (d, 1H, *J* = 15.9 Hz, H_{vinyl}), 8.65 (d, 1H, *J* = 5.0 Hz, $H6_{pyrim}$), 9.14 (s, 1H, $H2_{pyrim}$); ^{13}C NMR and JMOD (75 MHz, $CDCl_3$) δ 0.0 (CH_3), 96.4 (C), 104.8 (C), 118.9 (CH), 124.2 (C), 126.4 (CH), 127.5 (CH), 132.5 (CH), 135.6 (CH), 136.6 (C), 157.5 (CH), 158.9 (CH), 161.9 (C). HRMS (ESI/ASAP) *m/z* calculated for $C_{17}H_{19}N_2Si$ $[M+H]^+$: 279.1312, found 279.1312.

4-[2-(4-Ethynylphenyl)-vinyl]-pyrimidine (3f): Beige solid; obtained according to general procedure for deprotection of trimethylsilyl group; yield 83% (170 mg), mp: 154-156°C; ^{1}H NMR (300MHz, $CDCl_3$) δ 3.18 (s, 1H, $H_{C\equiv CH}$), 7.05 (d, 1H, *J* = 15.9 Hz, H_{vinyl}), 7.30 (d, 1H, *J* = 5.0 Hz, $H5_{pyrim}$), 7.50 (d, 2H, *J* =8.7 Hz, H_{Ph}), 7.55 (d, 2H, *J* =8.7 Hz, H_{Ph}), 7.85 (d, 1H, *J* = 15.9 Hz, H_{vinyl}), 8.69 (broad s, 1H, $H6_{pyrim}$), 9.17 (s, 1H, $H2_{pyrim}$); ^{13}C NMR and JMOD (75 MHz, $CDCl_3$) δ 78.9 (CH), 83.3 (C), 118.9 (CH), 123.1 (C), 126.5 (CH), 127.5 (CH), 132.6 (CH), 135.9 (C), 136.6 (CH), 157.3 (CH), 158.7 (CH), 162.0 (C). HRMS (ESI/ASAP) *m/z* calculated for $C_{14}H_{11}N_2$ $[M+H]^+$: 207.0917, found 207.0916.

4-[2-(5-Phenylethynyl-thiophen-2-yl)-vinyl]-pyrimidine (4a): Pale yellow solid; obtained according to general procedure and purified by column chromatography (SiO_2, Petroleum Ether/EtOAc 7/3); yield 69% (97 mg), mp: 114-116°C; ^{1}H NMR (300MHz, $CDCl_3$) δ 6.80 (d, 1H, *J* = 15.6 Hz, H_{vinyl}), 7.14 (d, 1H, *J* = 3.3 Hz, H_{thio}), 7.23-7.29 (m, 2H, H_{thio}+ $H5_{pyrim}$), 7.38-7.33 (m, 3H, H_{Ph}), 7.53-7.50 (m, 2H, H_{Ph}), 7.96 (d, 1H, *J* = 15.6 Hz, H_{vinyl}), 8.64 (broad s, 1H, $H6_{pyrim}$), 9.13 (s, 1H, $H2_{pyrim}$); ^{13}C NMR and JMOD (75 MHz, $CDCl_3$) δ 82.7 (C), 95.5 (C), 118.8 (CH), 122.5 (C), 125.0 (C), 125.2 (CH), 128.4 (CH), 128.8 (CH), 129.6 (CH), 129.8 (CH), 131.5 (CH), 132.8 (CH), 142.2 (C), 157.4 (CH), 158.8 (CH), 161.5 (C). HRMS (ESI/ASAP) *m/z* calculated for $C_{18}H_{13}N_2S$ $[M+H]^+$: 289.0800, found 289.0796.

4-{2-[5-(4-Methoxyphenylethynyl)-thiophen-2-yl]-vinyl}-pyrimidine (4b): Orange solid; obtained according to general procedure and purified by column chromatography (SiO_2,

Petroleum Ether/EtOAc 1/1); yield 54% (86 mg), mp: 115-117°C; ^{1}H NMR (300MHz, $CDCl_3$) δ 3.83 (s, 3H, H_{OMe}), 6.79 (d, 1H, J =15.6 Hz, H_{vinyl}), 6.88 (d, 2H, J =8.7 Hz, H_{Ph}), 7.13 (d, 1H, J =3.9 Hz, H_{thio}), 7.16 (d, 1H, J =3.9 Hz, H_{thio}), 7.22 (dd, 1H, J_1 = 5.0 Hz, J_2 = 1.0 Hz, $H5_{pyrim}$), 7.46 (d, 2H, J =8.7 Hz, H_{Ph}), 7.95 (d, 1H, J =15.6 Hz, H_{vinyl}), 8.64 (d, 1H, J = 5.0 Hz, $H6_{pyrim}$), 9.13 (s, 1H, $H2_{pyrim}$); ^{13}C NMR and JMOD (75 MHz, $CDCl_3$) δ 55.3 (CH_3), 81.5 (C), 95.6 (C), 114.1 (CH), 114.6 (C), 118.7 (CH), 124.9 (CH), 125.5 (C), 129.7 (CH), 129.6 (CH), 132.3 (CH), 133.0 (CH), 141.8 (C), 157.4 (CH), 158.8 (CH), 160.1 (C), 161.6 (C). HRMS (ESI/ASAP) *m/z* calculated for $C_{19}H_{15}N_2OS$ $[M+H]^+$: 319.0905, found 319.0900.

4-{2-[5-(4-*N*,*N*-dimethylaminophenylethynyl)-thiophen-2-yl]-vinyl}-pyrimidine (4c): yellow solid; obtained according to general procedure and purified by column chromatography (SiO_2, Petroleum Ether/EtOAc 1/1); yield 79% (131 mg), mp: 158-160°C; ^{1}H NMR (300MHz, $CDCl_3$) δ 3.00 (s, 6H, H_{NMe2}), 6.65(d, 2H, J =8.7 Hz, H_{Ph}), 6.77(d, 1H, J =15.6 Hz, H_{vinyl}), 7.12 (s, 2H, H_{thio}), 7.21 (d, 1H, J = 5.0 Hz, $H5_{pyrim}$), 7.39 (d, 2H, J =8.7 Hz, H_{Ph}), 7.95 (d, 1H, J =15.6 Hz, H_{vinyl}), 8.64 (broad s, 1H, $H6_{pyrim}$), 9.12 (s, 1H, $H2_{pyrim}$); ^{13}C NMR and JMOD (75 MHz, $CDCl_3$) δ 40.1 (CH_3), 80.9 (C), 97.3 (C), 109.0 (C), 111.8 (CH), 118.7 (CH), 124.5 (CH), 126.4 (C), 129.9 (CH), 130.0 (CH), 131.7 (CH), 132.7 (CH), 141.2 (C), 150.4 (C), 157.4 (CH), 158.8 (CH), 161.7 (C). HRMS (ESI/ASAP) *m/z* calculated for $C_{20}H_{18}N_3S$ $[M+H]^+$: 332.1221, found 332.1223.

4-{2-[5-(4-*N*,*N*-diphenylaminophenylethynyl)-thiophen-2-yl]-vinyl}-pyrimidine (4d): orange solid; obtained according to general procedure and purified by column chromatography (SiO_2, Petroleum Ether/EtOAc 1/1) followed by crystallization from CH_2Cl_2/*n*-heptane; yield 89% (202 mg), mp: 177-179°C; ^{1}H NMR (300MHz, $CDCl_3$) δ 6.79 (d, 1H, J =15.6 Hz, H_{vinyl}), 7.00 (d, 2H, J =8.7 Hz, H_{Ph}), 7.16-7.05 (m, 9H, H_{Ph} + H_{thio} + $H5_{pyrim}$), 7.37-7.28 (m, 6H, H_{Ph}), 7.97 (d, 1H, J =15.6 Hz, H_{vinyl}), 8.67 (broad s, 1H, $H6_{pyrim}$),

9.15 (s, 1H, $H2_{pyrim}$); ^{13}C NMR and JMOD (75 MHz, $CDCl_3$) δ 82.0 (C), 96.1 (C), 115.0 (C), 121.9 (CH), 123.8 (CH), 125.0 (CH), 125.2 (CH), 125.6 (C), 129.5 (CH), 128.8 (CH), 129.9 (CH), 132.3 (CH), 132.5 (CH), 141.8 (C), 147.1 (C), 148.5 (C), 157.4 (CH), 161.6 (C). HRMS (ESI/ASAP) *m/z* calculated for $C_{30}H_{22}N_3S$ $[M+H]^+$: 456.1534, found 456.1535.

4-[2-(5-Ethynylthiophen-2-yl)-vinyl]-pyrimidine (4f): Beige solid; obtained according to general procedure for deprotection of trimethylsilyl group; yield 56% (59 mg), mp: 136-138°C; ^1H NMR (300MHz, $CDCl_3$) δ 3.40 (s, 1H, $H_{C\equiv CH}$), 6.74 (d, 1H, J = 15.9 Hz, H_{vinyl}), 7.03 (d, 1H, J = 3.9 Hz, H_{thio}), 7.13 (d, 1H, J = 3.9 Hz, H_{thio}), 7.15 (d, 1H, J = 5.0 Hz, $H5_{pyrim}$), 7.87 (d, 1H, J = 15.9 Hz, H_{vinyl}), 8.59 (d, 1H, J = 5.0 Hz, $H6_{pyrim}$), 9.06 (s, 1H, $H2_{pyrim}$); ^{13}C NMR and JMOD (75 MHz, $CDCl_3$) δ 76.8 (CH), 83.4 (C), 118.9 (CH), 123.4 (C), 125.6 (CH), 129.3 (CH), 129.4 (CH), 134.0 (CH), 142.5 (C), 157.5 (CH), 158.8 (CH), 161.4 (C). HRMS (ESI/ASAP) *m/z* calculated for $C_{12}H_9N_2$ $[M+H]^+$: 213.0486, found 213.0484.

2-[2-(4-Phenylethynyl-phenyl)-vinyl]-quinoxaline (5a): yellow solid; obtained according to general procedure and purified by column chromatography (SiO_2, Petroleum Ether/EtOAc 3/7); yield 95% (157 mg), mp: 163-165°C; ^1H NMR (300MHz, $CDCl_3$) δ 7.37-7.28 (m, 4H, H_{Ph} + H_{vinyl}), 7.66-7.56 (m, 6H, H_{Ph}), 7.78-7.72 (m, 2H, $H6,7_{quinox}$), 7.87 (d, 1H, J =15.6 Hz, H_{vinyl}), 8.09 (d, 2H, J =8.7 Hz, $H5,8_{quinox}$), 9.04 (s, 1H, $H2_{quinox}$); ^{13}C NMR and JMOD (75 MHz, $CDCl_3$) δ 89.3 (C), 91.2 (C), 123.1 (C), 124.0 (C), 126.0 (CH), 127.4 (CH), 128.4 (CH), 128.5 (CH), 129.18 (CH), 129.22 (CH), 129.4 (CH), 130.4 (CH), 131.7 (CH), 132.1 (CH), 135.5 (CH), 135.8 (C), 141.7 (C), 142.5 (C), 144.5 (CH), 150.4 (C). HRMS (ESI/ASAP) *m/z* calculated for $C_{24}H_{17}N_2$ $[M+H]^+$: 333.1386, found 333.1386.

2-{2-[4-(4-Methoxyphenylethynyl)-phenyl]-vinyl}-quinoxaline (5b): yellow solid; obtained according to general procedure and purified by column chromatography (SiO_2, Petroleum Ether/EtOAc 3/7); yield 83% (150 mg), mp: 163-165°C; ^1H NMR (300MHz, $CDCl_3$) δ 3.86

(s, 3H, H_{OMe}), 6.90 (d, 2H, *J* =8.7 Hz, H_{Ph}), 7.41 (d, 1H, *J* =15.6 Hz, H_{vinyl}), 7.51 (d, 2H, *J* =8.7 Hz, H_{Ph}), 7.57 (d, 2H, *J* =8.7 Hz, H_{Ph}), 7.81-7.73 (m, 2H, H6,7_{quinox}), 7.88 (d, 1H, *J* =15.6 Hz, H_{vinyl}), 8.09 (d, 2H, *J* =8.7 Hz, H5,8_{quinox}), 9.04 (s, 1H, $H2_{quinox}$); ^{13}C NMR and JMOD (75 MHz, $CDCl_3$) δ 55.3 (CH_3), 88.1 (C), 91.4 (C), 114.1 (CH), 115.2 (C), 124.5 (C), 125.8 (CH), 127.4 (CH), 129.2 (CH), 129.4 (CH), 130.4 (CH), 131.9 (CH), 133.1 (CH), 135.5 (C), 135.7 (CH), 141.7 (C), 142.5 (C), 144.5 (CH), 150.5 (C), 159.8 (C). HRMS (ESI/ASAP) *m/z* calculated for $C_{25}H_{19}N_2O$ $[M+H]^+$: 363.1497, found 363.1498.

2-{2-[4-(4-*N*,*N*-dimethylaminophenylethynyl)-phenyl]-vinyl}-quinoxaline (5c): orange solid; obtained according to general procedure and purified by column chromatography (SiO_2, Petroleum Ether/EtOAc 3/7); yield 68% (127 mg), mp: 199-201°C; ^{1}H NMR (300MHz, $CDCl_3$) δ 3.00 (s, 6H, H_{NMe2}), 6.67 (d, 2H, *J* =8.7 Hz, H_{Ph}), 7.38 (d, 1H, *J* =15.6 Hz, H_{vinyl}), 7.43 (d, 2H, *J* =8.7 Hz, H_{Ph}), 7.54 (d, 2H, *J* =8.7 Hz, H_{Ph}), 7.62 (d, 2H, *J* =8.7 Hz, H_{Ph}), 7.79-7.68 (m, 2H, H6,7_{quinox}), 7.85 (d, 1H, *J* =15.6 Hz, H_{vinyl}), 8.08 (d, 2H, *J* =8.7 Hz, H5,8_{quinox}), 9.03 (s, 1H, $H2_{quinox}$); ^{13}C NMR and JMOD (75 MHz, $CDCl_3$) δ 40.2 (CH_3), 87.5 (C), 92.8 (C), 109.8 (C), 111.8 (C), 125.1 (C), 125.5 (CH), 127.4 (CH), 129.2 (CH), 129.3 (CH), 130.3 (CH), 131.7 (CH), 132.8 (CH), 135.0 (C), 135.8 (CH), 141.6 (C), 142.5 (C), 144.5 (CH), 150.3 (C), 150.6 (C). HRMS (ESI/ASAP) *m/z* calculated for $C_{26}H_{22}N_3$ $[M+H]^+$: 376.1808, found 376.1806.

2-{2-[4-(4-*N*,*N*-diphenylaminophenylethynyl)-phenyl]-vinyl}-quinoxaline (5d): yellow solid; obtained according to general procedure and purified by column chromatography (SiO_2, Petroleum Ether/EtOAc 3/7); yield 72% (180 mg), mp: 213-215°C; ^{1}H NMR (300MHz, $CDCl_3$) δ 7.14-7.00 (m, 8H, H_{Ph}), 7.31-7.26 (m, 4H, H_{Ph}), 7.42-7.37 (m, 3H, H_{Ph} + H_{vinyl}), 7.55 (d, 2H, *J* =8.7 Hz, H_{Ph}), 7.63 (d, 2H, *J* =8.7 Hz, H_{Ph}), 7.79-7.68 (m, 2H, H6,7_{quinox}), 7.87 (d, 1H, *J* =15.6 Hz, H_{vinyl}), 8.09-8.05 (m, 2H, H5,8_{quinox}), 9.04 (s, 1H, $H2_{quinox}$); ^{13}C NMR and

JMOD (75 MHz, $CDCl_3$) δ 88.6 (C), 91.7 (C), 115.8 (C), 122.2 (CH), 123.6 (CH), 124.5 (C), 125.1 (C), 125.8 (CH), 127.4 (CH), 129.2 (CH), 129.3 (CH), 129.4 (CH), 130.3 (CH), 131.9 (CH), 132.6 (CH), 135.5 (C), 135.7 (CH), 141.7 (C), 142.5 (C), 144.5 (CH), 147.2 (C), 148.1 (C), 150.5 (C). HRMS (ESI/ASAP) *m/z* calculated for $C_{36}H_{26}N_3$ $[M+H]^+$: 500.2121, found 500.2119.

2-[2-(4-Trimethylsilylethynyl-phenyl)-vinyl]-quinoxaline (5e): Beige solid; obtained according to general procedure and purified by column chromatography (SiO_2, Petroleum Ether/EtOAc 7/3); yield 75% (123 mg), mp: 123-125°C; ^{1}H NMR (300MHz, $CDCl_3$) δ 0.26 (s, 9H, H_{SiMe3}), 7.37 (d, 1H, J = 16.2 Hz, H_{vinyl}), 7.51 (d, 2H, J = 8.4 Hz, H_{Ph}), 7.59 (d, 2H, J = 8.4 Hz, H_{Ph}), 7.79-7.68 (m, 2H, H6,7$_{quinox}$), 7.84 (d, 1H, J =16.2 Hz, H_{vinyl}), 8.09-8.04 (m, 2H, H5,8$_{quinox}$), 9.02 (s, 1H, H2$_{quinox}$); ^{13}C NMR and JMOD (75 MHz, $CDCl_3$) δ 0.0 (CH_3), 96.3 (C), 104.9 (C), 123.9 (C), 126.2 (CH), 127.3 (CH), 129.2 (CH), 129.3 (CH), 129.5 (CH), 130.4 (CH), 132.5 (CH), 133.2 (CH), 135.6 (CH), 136.1 (C), 141.7 (CH), 142.6 (C), 144.5 (CH), 150.4 (C). HRMS (ESI/ASAP) *m/z* calculated for $C_{21}H_{21}N_2Si$ $[M+H]^+$: 329.1469, found 329.1469.

2-[2-(4-Ethynylphenyl)-vinyl]-quinoxaline (5f): Beige solid; obtained according to general procedure for deprotection of trimethylsilyl group; yield 84% (215 mg), mp: 123-125°C; ^{1}H NMR (300MHz, $CDCl_3$) δ 3.19 (s, 1H, $H_{C\equiv CH}$), 7.38 (d, 1H, J = 16.2 Hz, H_{vinyl}), 7.54 (d, 2H, J = 8.4 Hz, H_{Ph}), 7.62 (d, 2H, J = 8.4 Hz, H_{Ph}), 7.79-7.70 (m, 2H, H6,7$_{quinox}$), 7.85 (d, 1H, J =16.2 Hz, H_{vinyl}), 8.09-8.06 (m, 2H, H5,8$_{quinox}$), 9.03 (s, 1H, H2$_{quinox}$); ^{13}C NMR and JMOD (75 MHz, $CDCl_3$) δ 72.2 (CH), 78.8 (C), 122.8 (C), 126.3 (CH), 127.3 (C), 129.2 (CH), 129.5 (CH), 130.4 (CH), 132.6 (CH), 135.4 (CH), 136.4 (C), 141.4 (C), 142.5 (C), 144.5 (CH), 150.3 (C). HRMS (ESI/ASAP) *m/z* calculated for $C_{18}H_{13}N_2$ $[M+H]^+$: 257.1073, found 257.1075.

Supporting Information Available: copies of ^{1}H NMR and ^{13}C NMR spectra for all compounds, UV/Vis and PL data in toluene, solvatochromic range between hexane/heptane and dichloromethane for compounds **5c** and **5d** and their analogues as well as plots of emission maxima versus $E_T(30)$.

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