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2-Arylvinylpyrimidines versus 4-arylvinylpyrimidines: synthesis and comparison of the optical properties

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ABSTRACT

Condensation of donor-substituted aldehydes on methylpyrimidine led to two series of fluorescent molecules depending on the position of the methyl group. Whereas highly emissive 4-arylvinylpyrimidine derivatives are well-known, this is the first example of fluorescent 2-arylvinylpyrimidine compounds. The optical properties of the two families have been thoroughly compared. Whereas the series derived from 2-methylpyrimidine exhibit a blue shift in absorption and emission in comparison with 4-arylvinylpyrimidine, the influence of the position is less predictable on the fluorescence quantum yield. These compounds also exhibit halochromism: when adding acid, a bathotromic shift is observed in absorption whereas an increase of the fluorescence intensity which is red-shifted except for amino derivatives (a progressive quench of emission is observed in these cases). An emission solvatochromism study has shown that a higher intramolecular charge transfer seems to occur in 2-arylvinylpyrimidines than in 4-arylvinylpyrimidines.

During the past decades, there has been a great interest in the synthesis of π-conjugated pyrimidine derivatives due to the potential applications in optoelectronics.[1] Indeed the pyrimidine, which is a highly π-deficient aromatic heterocycle, can be used as electron withdrawing part in push–pull structures for intramolecular charge transfer (ICT). An important ICT is a key parameter to obtain luminescent and nonlinear optical (NLO) properties.

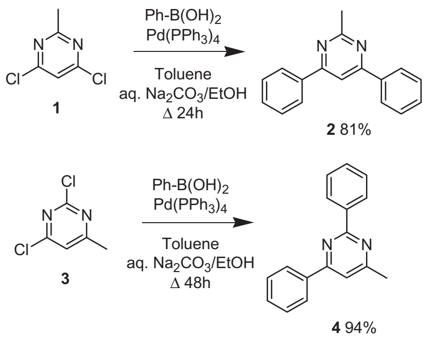
Since their first design by Vanden Eynde and co-workers in 2001,[2] 4,6-diarylvinylpyrimidines have become a well established design for luminescent dyes with sensing applications,[3] second order NLO materials,[4] and two photon absorption (TPA) chromophores.[5] Recently, we have also described 4-arylvinylpyrimidines that can be used as metal cation sensors,[6] duplex DNA sensors,[7] and second order NLO chromophores.[8]

Even if some 2-arylvinylpyrimidines have been described for their biological activities,[9] to the best of our knowledge, the photophysical properties of these derivatives have not been studied.

In continuation of our work dedicated to diazine dyes, the aim of this Letter is to describe the synthesis and photophysical properties of two series of 2- and 4-arylvinylpyrimidines. The two families of molecules will be thoroughly compared in terms of absorption and emission properties.

Two main methods have been described for the synthesis of (*E*)-arylvinylpyrimidines: the use of cross coupling reactions with halogenopyrimidines[10] and the condensation of aldehyde with methylpyrimidines.[2,3a,4,5a–f,6a,8] The latter approach has the advantages of a wide range of commercially available aldehydes and the use of environmentally friendly conditions in most cases.

Taking into account the fact that 2-methylpyrimidine is not commercially available or easy to synthesize, it has been chosen to work with diphenyl derivatives **2** and **4**. These compounds can be easily obtained by Suzuki cross-coupling reaction[11] from easily available 4,6-dichloro-2-methylpyrimidine **1** and 2,4-dichloro-6-methylpyrimidine **3** (Scheme 1). It should be noted that the π-electron deficient character of the pyrimidine ring makes the oxidative addition of palladium to a chlorine–carbon bond in position 2, 4, and 6 easier without the use of specialized and expensive ligands.[12] Nevertheless the addition of palladium is a bit more



Scheme 1.

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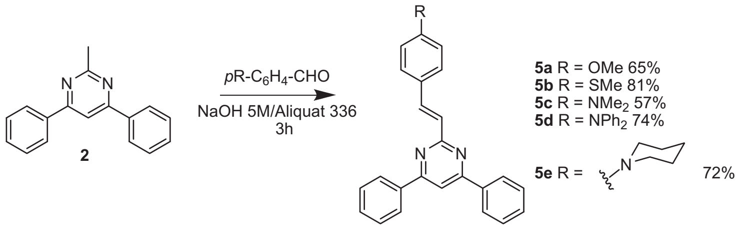
difficult in position 2 and requires a longer reaction time (24 h for compound **2** vs 48 h for compound **4**).[13]

The synthesis of arylvinylpyrimidines **5** and **6** has been carried out by condensation reaction between methylpyrimidines **2** and 3 *para*-substituted benzaldehyde in boiling aqueous 5 M NaOH using Aliquat® 336 as a phase transfer catalyst according to the method initially described by Vanden Eynde (Schemes 2 and 3).[14] Compounds **5** and **6** have been obtained in moderate to good yield. It should be noted that no significant difference in reactivity has been observed between methyl in positions 2 and 4 of the pyrimidine ring.

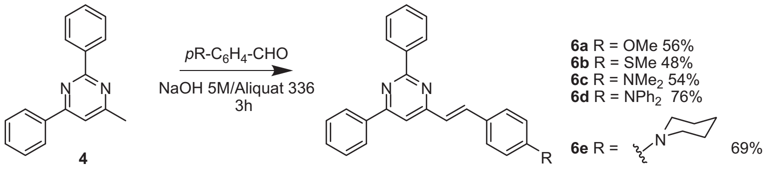
The UV–vis and photoluminescence (PL) spectroscopic data of compounds **5** and **6** measured in dichloromethane at 25 °C are presented in Table 1. Analyses have been carried out using low concentration solutions (1.0×10^{-5} to 3.0×10^{-5} M for UV/vis spectra and 1.0×10^{-6} to 3.0×10^{-6} M for PL spectra). As an example, the spectra for derivatives **5d**, **6a,** and **6d** 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 the compounds exhibit two absorption bands. The most energetic one is located in the 252–276 nm range, the less energetic one (λ_{abs} = 326–411 nm) is attributed to a charge transfer transition. Compounds **6** are slightly red shifted in comparison with 4-arylvinylpyrimidines that are not substituted in positions 2 and 6 of the pyrimidine ring.[8] It should be noted that the less energetic band is blue shifted (λ_{abs} = 16–25 nm) for 2-arylvinylpyrimidines **5** in comparison with 4-arylvinylpyrimidines **6**. This is a bit more difficult to rationalize the emission results: Whereas some subtituents (SMe and NPh_2) lead to an important hypsochromic shift (up to 30 nm) on the emission band of the 2-arylvinylpyrimidines (**5b** and **5d**) in comparison with 4-arylvinylpyrimidines (**6b** and **6d**), the other substituents (OMe, NMe_2 and piperidinyl) do not conduct to significant modification of the emission maxima. In terms of emission intensity, 2-arylvinylpyrimidines **5** exhibit lower fluorescent quantum yield compared with 4-arylvinylpyrimidines **6**, excepted for the diphenylamino derivatives: in that case the 2-arylvinylpyrimidines **5d** (ϕ_F = 0.71) exhibit a two-time higher quantum yield than the 4-arylvinylpyrimidines **6d**. Taking into account the absorption and the emission shifts, the Stokes shifts are generally higher for compounds **5** than for compound **6**.

In previous studies,[3a,6a,7,8] we demonstrated the ability of related 4-(arylvinyl)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 (**5d** and **6d**). Dichloromethane solutions of these compounds underwent a significant color change in the presence of TFA (10^{-2} M) (Fig. 2). As expected, the compounds exhibit a bathochromic shift of their absorption bands upon protonation due to an increased charge transfer from the donors to the pyrimidinium moiety. This color change is fully reversible by neutralization with a base such as Et_3N or KBu^tO.



Scheme 2.



Scheme 3.

Table 1
UV/vis and photoluminescence (PL) data

Compd[a]	UV/vis (λ_{max}, nm) (ε, mM^{-1} cm^{-1})	PL (λ_{max}, nm)	Φ_F[b]	Stokes shift[c] (cm^{-1})
5a	276 (28.2), 326 (25.1)	426	0.009	7201
5b	263 (27.4), 337 (16.5)	429	0.024	6364
5c	261 (35.4), 383 (23.9)	519	0.062	6842
5d	276 (31.2), 395 (19.9)	499	0.71	5276
5e	260 (40.3), 376 (31.0)	524	0.057	7511
6a	252 (49.3), 351 (20.0)	430	0.002	5234
6b	261 (42.0), 359 (15.6)	449	0.044	5583
6c	260 (41.1), 406 (26.2)	520	0.14	5400
6d	268 (24.2), 411 (16.2)	525	0.35	5283
6e	260 (33.6), 397 (22.5)	522	0.22	6031

[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 (Φ_F = 0.54).
[c] Calculated using the less energetic absorption band.

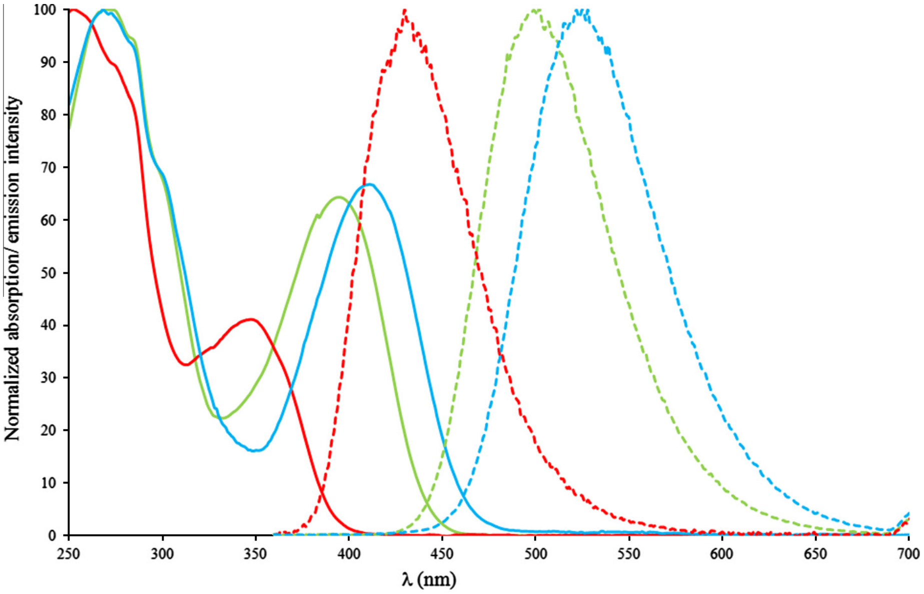


Figure 1. Normalized UV/vis (solid line) and emission spectra (brocken line) of compounds **5d** (green), **6a** (red) and **6d** (blue).

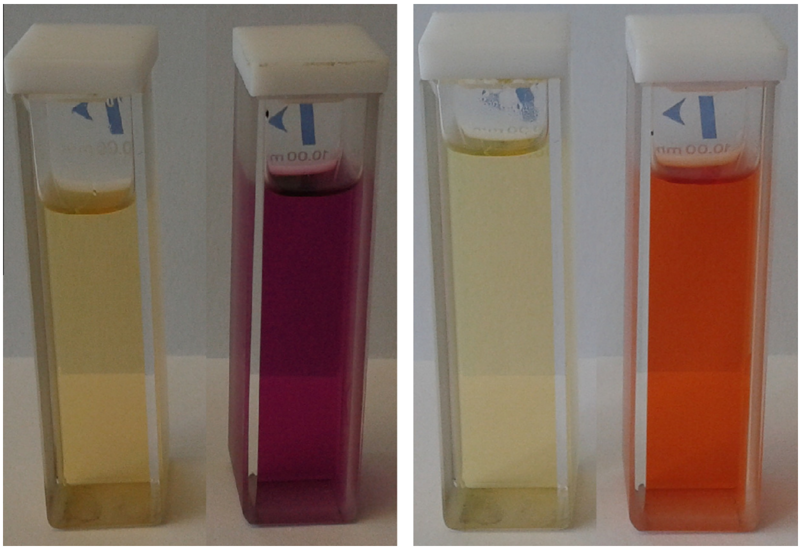


Figure 2. Color change of CH_2Cl_2 solutions of compounds **5d** (left) and **6d** (right) ($c = 10^{-3}$ M in the presence of 10^{-2} M TFA).

The changes in the UV–vis spectra of **5d** and **6d** upon progressive addition of acid are illustrated in Figures 3 and 4. The spectra show the progressive attenuation of the absorption band for the neutral compound on increasing the concentration of acid, whereas a new red-shifted band corresponding to the protonated species appeared. It should be noted that for compound **6d**, for a concentration of TFA = 10^{-2} M and even more for a concentration of TFA = 10^{-1} M, absorption band is red-shifted probably due to the impact of the increasing solvent polarity (CH_2Cl_2 + TFA) on the highly polar protonated compound.[15] As described in Table 2, a red shift of the absorption band is observed upon the addition of TFA ($c = 10^{-2}$ M) except for compounds **6c** and **6e** bearing the protonable amino group: in these cases a blue shift of the absorption band is observed. Such a phenomenon has been already observed with arylvinyldiazine substituted with amino groups.[8,16] It should be noted that the same blue shift is not observed for compounds **5c** and **5e**.

In terms of emission, the progressive addition of TFA leads to the progressive quench of the luminescence of amino derivatives whereas the progressive addition of TFA in solution of methoxy and thiomethyl derivatives inducts an increase of the fluorescence intensity (see Fig. 5). No significant difference is observed with emission behavior between compounds **5** and **6** upon the addition of acid.

In an effort to gain further insight into the photophysical process within these push–pull molecules, we investigated the emission behaviors of compounds **5** and **6** in different aprotic solvents. The results of these investigations are summarized in Table 3. As an example the emission spectra in various solvents for compound **5d** are shown in Figure 6. For all compounds, a bathochromic shift of the emission band is observed with increasing solvent polarity as predicted by Dimroth–Reichardt polarity parameter ($\Delta E_T(30)$).[17] In contrast, the absorption wavelength is not significantly shifted. Broad structureless emission and larger Stokes shifts were observed for polar solvents. The correlation of the emission maxima with $\Delta E_T(30)$ is represented in Figure 7 and in Supporting information and was found to be positively linear for all the compounds. This solvatochromic behavior, which re-

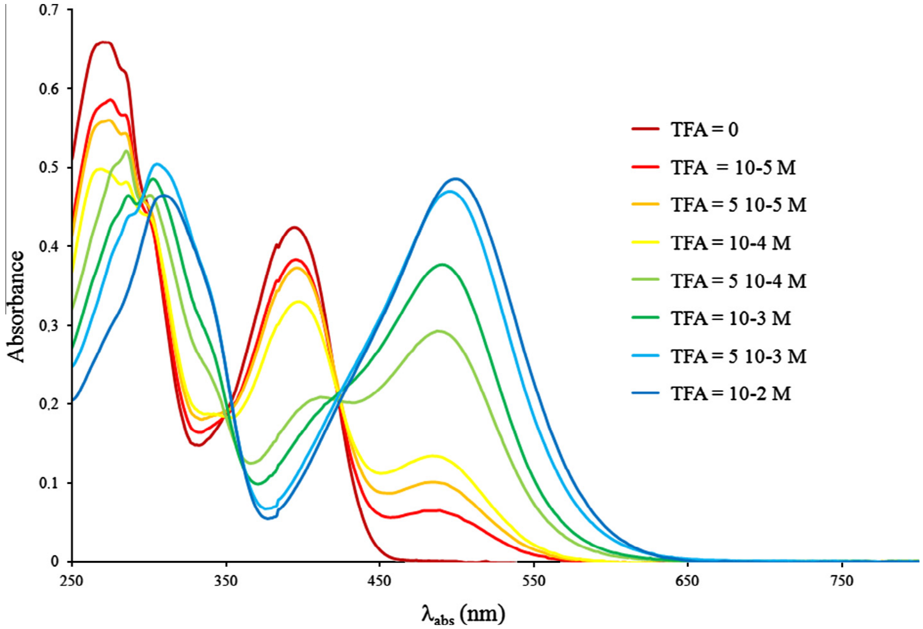


Figure 3. Change in the absorption spectra of **5d** ($c = 2 \times 10^{-5}$ M) upon the addition of TFA (10^{-5} to 10^{-2} M).

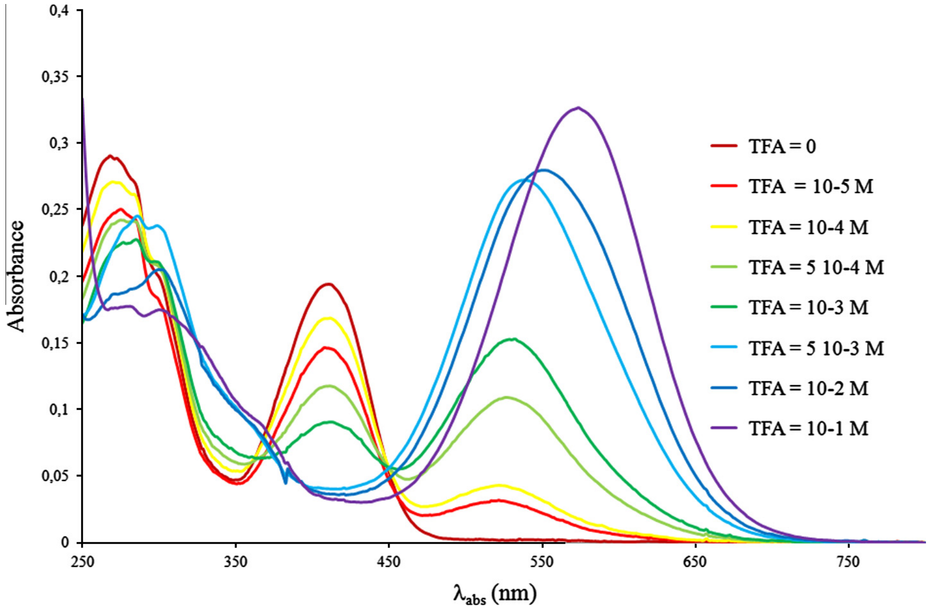


Figure 4. Change in the absorption spectra of **6d** ($c = 1.2 \times 10^{-5}$ M) upon the addition of TFA (10^{-5} to 10^{-1} M).

Table 2
Comparison of the position of the less energetic absorption band upon the addition of TFA

	CH_2Cl_2[a]	TFA 10^{-2} M in CH_2Cl_2[a]
5a	326	402
5b	337	424
5c	383	489
5d	395	507
5e	376	484
6a	351	431
6b	359	451
6c	406	370
6d	411	555
6e	397	370

[a] All spectra were recorded at room temperature at $c = 1.0 \times 10^{-5}$ to 3.0×10^{-5} M.

sults 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.[18] When comparing for each substituent the emission solvatochromic range expressed as a wave number for 2-arylvinylpyrimidines **5** and 4-arylvinylpyrimidines **6**, it appears that this range is much higher for compounds **5** than for compounds **6**. Moreover the slope of the emission maxima versus $\Delta E_T(30)$ is higher for 2-arylvinylpyrimidine **5** than for 2-arylvinylpyrimidine **6** for each substituent. This seems to indicate that the internal charge transfer is more important in compounds **5** than in compounds **6** and therefore 2-substituted pyrimidine is a better electron-accepting group than 4-substituted pyrimidine. It should be noted that in polar solvent for amino derivatives **5c**

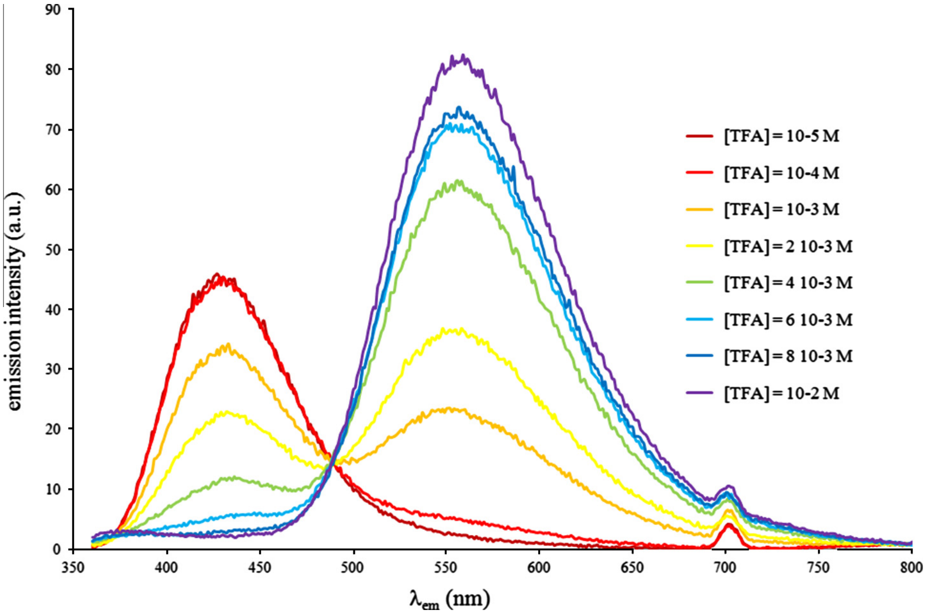


Figure 5. Change in the emission spectra of **5a** ($c = 2 \times 10^{-6}$ M) upon the addition of TFA (10^{-5} to 10^{-2} M), excitation at 350 nm.

Table 3
Emission solvatochromic range of arylvinylpyrimidines **5** and **6** in various aprotic solvents

	n-Heptane $E_T(30) = 0.0$[a]	THF $E_T(30) = 27.2$[a]	CH$_2$Cl$_2$ $E_T(30) = 40.7$[a]	Acetone $E_T(30) = 42.2$[a]	DMSO $E_T(30) = 59.0$[a]	ν[b] in cm^{-1}
5a	392	425	426	435	463	3912
5b	399	426	429	440	460	3323
5c	441	512	519	568	587	5070
5d	420	480	499	504	526	4790
5e	450	518	524	563	591	5301
6a	403	428	430	436	456	2884
6b	415	445	449	459	475	3044
6c	448	508	520	531	554	4270
6d	485	508	525	528	551	2469
6e	461	511	522	535	552	3576

[a] Dimroth–Reichardt polarity parameter, J mol^{-1}.
[b] $\nu = \nu(\text{heptane}) - \nu(\text{DMSO})$.

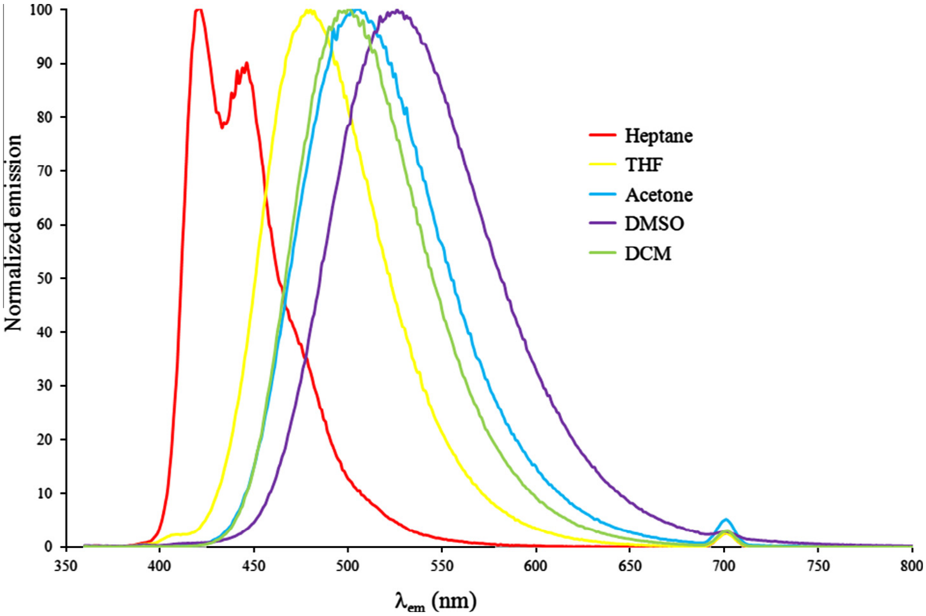


Figure 6. Normalized emission of compound **5d** in various solvents ($c = 2 \times 10^{-6}$ M).

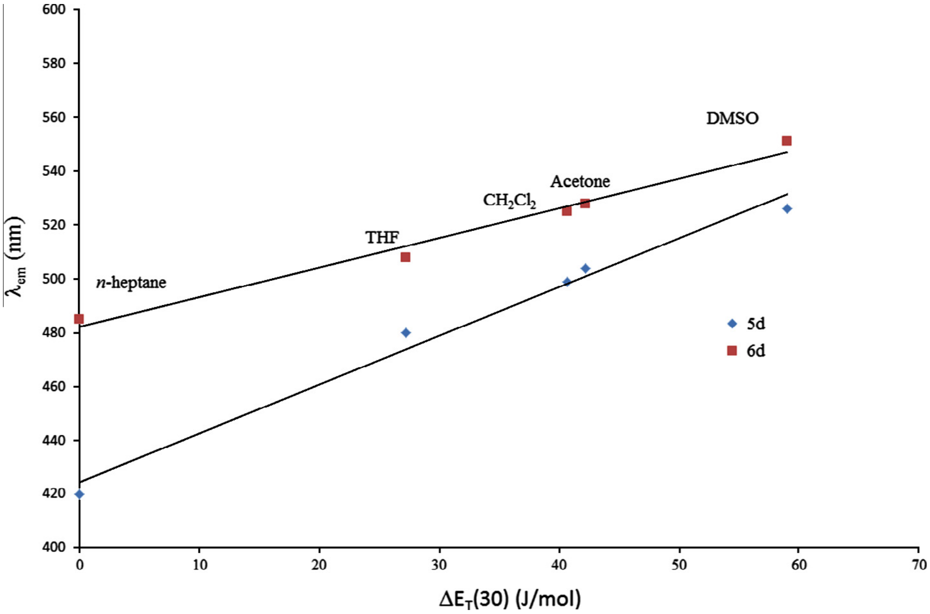


Figure 7. Emission wavelength (λ_{max}) as a function of Dimroth–Reichart polarity parameter for compounds **5d** and **6d**.

and **5d** the emission intensity decreases dramatically, it was not observed with the other compounds studied.

To conclude, we have efficiently synthesized two series of donor substituted arylvinylpyrimidines from 4-methyl and 2-methylpyrimidine derivatives. This is the first example for condensation of aldehyde on 2-methylpyrimidine derivatives. We have shown that the absorption and emission maxima are generally blue shifted in case of 2-arylvinylpyrimidines **5** when compared with 4-arylvinylpyrimidines **6**. The influence of the position is less predictable in terms of quantum yield. Similar halochromism phenomena have been observed in the two series of molecules. An emission solvatochromism study has shown that a higher intramolecular charge transfer seems to occur in 2-arylvinylpyrimidines **5** than in 4-arylvinylpyrimidines **6**. Donor substituted 2-arylvinylpyrimidines seem therefore to be really interesting structures for NLO properties. Investigations in this direction are currently being carried out.

Acknowledgments

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Supplementary data

Supplementary data (experimental details, spectroscopic data, copies of ^{1}H and ^{13}C.) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.06.040.

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