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V-Shaped 4,6-Bis(arylvinyl)pyrimidine Oligomers: Synthesis and Optical Properties

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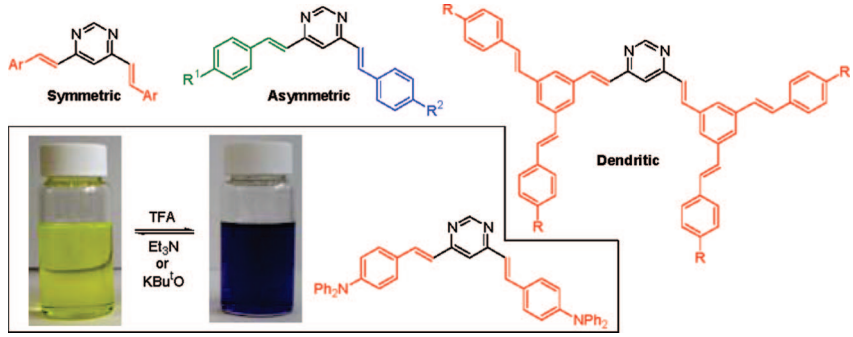

A series of V-shaped 4,6-bis(arylvinyl)pyrimidines have been efficiently prepared by aldol condensation between 4,6-dimethylpyrimidine and the appropriate aromatic aldehyde. The methodology also proved successful when dendritic first generation poly(phenylenevinylene) aldehydes were used. Moreover, asymmetrically functionalized molecules were also obtained by the stepwise incorporation of arms in a controlled manner. The optical absorption and emission properties of these systems were studied in different solvents and media. The materials display strong emission solvatochromism that is reflected by a large red shift in their fluorescence emission maxima on increasing the solvent polarity. This change is accompanied by a successive decrease in fluorescence intensity. This behavior suggests a highly polar emitting state, which is characteristic of compounds that undergo an internal charge transfer upon excitation. The abilities of these molecules to function as colorimetric and luminescence pH sensors were demonstrated with dramatic color changes and luminescence switching upon the introduction of acid.

Introduction

Organic polymers with good photoluminescent responses are promising candidates for photonic, electronic, and optoelectronic applications.[1] These systems usually have in common a fully conjugated backbone with alternate double and single (or triple and single) bonds along a chain. Numerous technological devices have been developed that incorporate this type of material. Poly(*p*-phenylenevinylenes) (PPVs)[2] are the most commonly used family in light-emitting or light-sensitive devices as their electro-optical properties are known to depend on the chain length and the presence of substituents. Thus, PPVs dominate the field of PLEDs (polymer light-emitting diodes) and similar applications, despite their moderate stability and the sensitive process needed to obtain good-quality devices.

In this context, π-conjugated oligomers have also been intensively studied, and there are numerous reasons for working with such short molecules. For example, they are more soluble

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in common organic solvents than homologous polymers, which makes it possible to analyze them readily by standard spectroscopic techniques. The energies for optical transitions of short oligophenylenevinylenes are higher than those for longer chains,[3] and moreover, the incorporation of *meta* linkages in the phenylenevinylene backbone lowers the molecular conjugation. Both of these effects allow the system to emit blue light,[3,4] the primary color that is the hardest to obtain with PLEDs.

Among these oligomers, molecules with a D-π-A or D-π-A-π-D structure (where D is an electron-donating group, A an electron-accepting group, and π a conjugating moiety) are of high interest due to their fluorescence properties with internal charge transfer (ICT) and as chromophores for second- and third-order nonlinear optics (NLO).[5] The pyrimidine ring is an excellent candidate to be incorporated in such structures. Indeed, this heterocycle has a high electron-withdrawing character, significant aromaticity that can lead to highly conjugated molecules, as well as basic and potential ligand properties that can also be used to modulate the optoelectronic properties of molecules. Oligomers that contain pyrimidine rings have been used as liquid crystals,[6] n-type semiconductors,[7] components of electroluminescent diodes,[8] fluorescent molecules,[9] and two-photon absorption chromophores.[10]

On the other hand, dendritic poly(phenylenevinylenes), also called stilbenoid dendrimers, represent an important group within this class of material. Several different studies have been published to date concerning the synthesis and properties of these materials.[11] For example, such compounds have been used successfully as charge transporting,[12] light-emitting,[13] and electron-transfer materials.[14] It has also been demonstrated that phenylenevinylene dendritic arms can function as light-harvesting antennae.[13b]

We describe here the synthesis and characterization of a novel series of V-shaped molecules with a 4,6-divinylpyrimidine core and phenylenevinylene arms bearing electron-donating and/or electron-withdrawing groups. The influence of the nature of the electroactive substituents on the optical absorption and emission properties was examined along with the fluorosolvatochromism and pH sensitivity. The incorporation of PPV dendritic structures on the 4,6-divinylpyrimidine core was also assessed in order to combine the properties of both types of chromophores.

Results and Discussion

Preparation of Divinylpyrimidines. Two main methods have been described for the synthesis of (*E*)-vinylpyrimidines: the Suzuki cross-coupling reaction of potassium alkenyltrifluoroborates with chloropyrimidines[15] and the condensation of aldehydes with methylpyrimidines.[16] The latter approach has the advantages of a wide range of commercially available aldehydes and the use of environmentally friendly conditions in most cases. In this way, a large variety of dicondensation products could be readily obtained by aldol condensation between 4,6-dimethylpyrimidine and the corresponding aromatic aldehyde (Table 1). Reactions were carried out in boiling aqueous 5 M NaOH (1 M for **2e**) using Aliquat 336 as a catalyst, according to a previously reported procedure.[16a−c] The experimental protocol is straightforward and rather economical since it does not require any organic solvent. All of the products were obtained in good yields after recrystallization—except for the naphthalene and anthracene derivatives, which suffered from difficulties in the purification process.

In order to increase the electronic delocalization along each arm, pentacyclic V-shaped oligomers **3a**,**b** and **4** were also synthesized in good yields by Suzuki cross-coupling of bromo derivatives **2d** and **2h**, respectively, with the appropriate boronic acids (Scheme 1).

Methods for the preparation of this class of oligomer in an asymmetrically functionalized fashion (i.e., bearing differently substituted phenylenevinylene arms) have not been described in the literature to date. In our case, this goal was achieved by the stepwise incorporation of arms in a controlled manner. In the aforementioned procedure, the reaction with only 1 equiv of aldehyde proved unsuccessful in giving the corresponding monocondensation derivatives; however, when KBu^{t}O was used as the base in refluxing THF, vinylpyrimidines **5a**,**b** could be obtained. Although the corresponding dicondensation products were also present in the crude mixtures, the desired compounds could be separated by column chromatography in moderate yields. However, it was not possible to obtain a pure sample of **5b**, which was always accompanied by ca. 10% of the dicondensation derivative **2b**. As a result, this material was used in the next step without further purification. This step involved a second condensation reaction with a different aldehyde to afford the asymmetric divinylpyrimidines **6a−c** in good isolated yields (Scheme 2).

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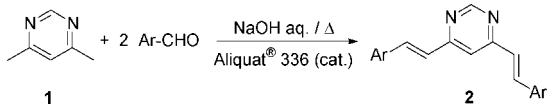
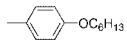
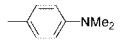
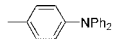
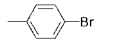
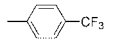
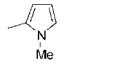
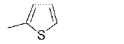
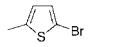
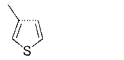
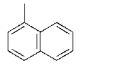
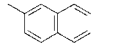
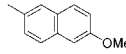
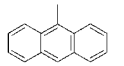
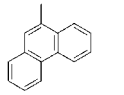
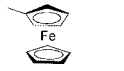
TABLE 1. Condensation of 4,6-Dimethylpyrimidine with Aromatic Aldehydes



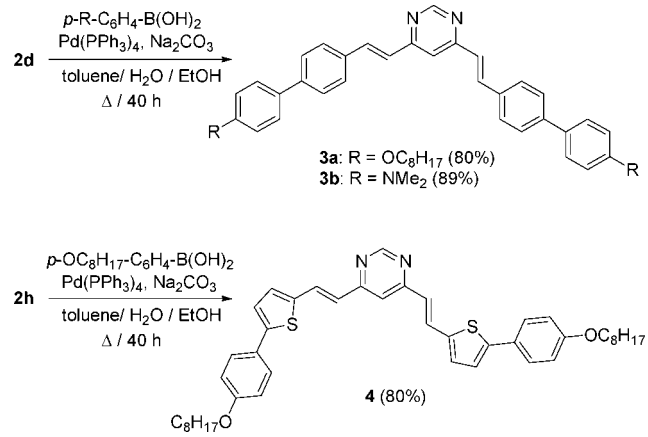
1 2

Compd	Ar	Isolated yield (%)
2a		81
2b		77
2c		62
2d		70
2e		74
2f		95
2g		93
2h		78
2i		90
2j		30
2k		40
2l		37
2m		48
2n		86
2o		95

All new compounds were characterized using a variety of analytical techniques. The overall purities of these compounds were confirmed by elemental analysis. NMR experiments proved very useful to confirm the structures of the compounds (see 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 ^{1}H NMR spectra ($J \sim 16$ Hz). The low solubility of compounds **2n**, **3a**, and **4** required the addition of TFA to the NMR tube in order to acquire the spectra. Well-resolved signals for the corresponding protonated species were obtained in all cases. It is also worth noting the line broadening observed at room temperature for compound **2m**. The signals for these compounds appeared well-resolved upon heating the sample at 60 °C, a phenomenon that is probably due to a tendency for this kind of compound to aggregate.

These materials are perfectly stable in the solid state and could be stored without the need for any special precautions. However, it should be noted that some samples underwent partial decomposition and/or *cis*−*trans* isomerization when they were allowed to stand in chloroform solution at room temperature for several days, especially those compounds with strongly electron-donating amino groups.

SCHEME 1. Suzuki Cross-Coupling Reaction of Bromo Derivatives 2d and 2h



Preparation of Dendritic PPV Pyrimidines. Having verified the general accessibility of divinylpyrimidines through simple aromatic aldehydes, the corresponding dendritic materials were synthesized by following a similar protocol in aqueous media. The appropriate first generation dendritic PPV aldehydes **7a**,**b** were easily obtained by reaction of the corresponding iodo derivatives[17] with Bu^{n}Li at −78 °C followed by quenching with DMF.[13e,18] These two compounds were then reacted with 4,6-dimethylpyrimidine **1** to provide the expected dendritic pyrimidines **8a**,**b** (Scheme 3).

The long alkyl chain in dendrimer **8a** led to a reasonable level of solubility in a variety of organic solvents such as THF, chloroform, and dichloromethane. In contrast, the presence of the terminal CF_3 groups lower the solubility of the system, and dendrimer **8b** is only sparingly soluble in THF. The ^{1}H and ^{13}C NMR spectra are consistent with these compounds having double bonds with a *trans* configuration [^3J(H,H) $\sim$ 16 Hz]. The MS and HRMS data also support the formation of the desired dendrimers.

UV/Vis and PL Spectroscopy. The optical properties of the synthesized divinylpyrimidines were investigated by UV/vis and photoluminescence (PL) spectroscopy on CH_2Cl_2 solutions at room temperature. The data obtained are summarized in Table 2. All compounds were photostable and did not undergo *cis*−*trans* isomerization under the analysis conditions. The *meta* arrangement through which the different units are linked prevents efficient delocalization throughout the conjugated backbone, and as a result, all of these compounds show absorption wavelengths (λ_{max}) in the UV or visible region (330−492 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.[9d]

The materials are also fluorescent and strongly emit light when irradiated, showing a typical response in the visible region (407−592 nm). Only compound **2o** is nonemissive, and this

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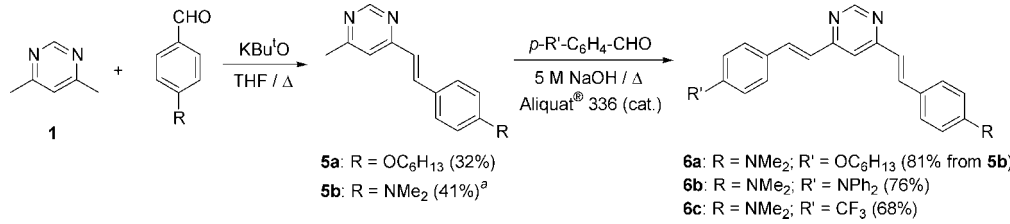
SCHEME 2. Preparation of Asymmetric Divinylpyrimidines



[a] Compound **5b** was isolated accompanied by ca. 10% of the dicondensation derivative **2b**.

SCHEME 3. Synthesis of Dendritic PPV Pyrimidines

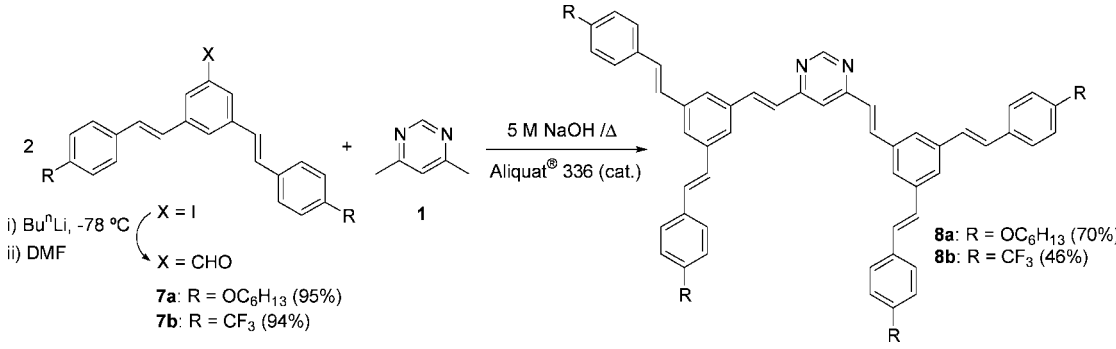


TABLE 2. UV/Vis and Photoluminescence (PL) Data

compd[a]	UV/vis (CH_2Cl_2) λ_{max}, nm (ε, M^{-1} cm^{-1})	PL (CH_2Cl_2) λ_{max}, nm	Φ_F[b]	Stokes shift, cm^{-1}
2a	296 (17000), 369 (35600)	444	0.06[c]	4578
2b	429 (42100)	530	0.40[c]	4442
2c	301 (38900), 427 (47600)	540	0.55[c]	4901
2d	290 (41300), 350 (26400)	407	0.01[d]	4001
2e	280 (38500), 341 (30200)	393, 419	<0.01[e]	3880[f]
2f	289 (95200), 408 (29700)	496	0.14[c]	4349
2g	304 (12700), 370 (31900)	444	<0.01[c]	4505
2i	287 (21800), 349 (33300)	410	0.03[d]	4263
2j	256 (31600), 357 (27100)	451	0.11[c]	5838
2k	276 (20300), 332 (26200)	424	0.08[c]	6536
2l	263 (26500), 283 (27100), 380 (27100)	470	0.37[c]	5039
2m	410 (27300)	525	0.02[c]	5342
2n	366 (28500)	457	0.12[c]	5440
2o	258 (15900), 329 (23400), 492 (5300)			
3a	373 (60500)	483	0.59[c]	6106
3b	309 (49200), 407 (71600)	592	0.26[c]	7678
4	423 (47800)	529	0.14[c]	4737
6a	413 (35900)	543	0.42[c]	5797
6b	301 (19200), 428 (39500)	545	0.45[c]	5012
6c	317 (25000), 421 (28400)	586	0.05[c]	6688
8a	330 (105400)	508	0.10[d]	10344

[a] All spectra were recorded at room temperature at $c = 2$ mg/L (1.8×10^{-6} to 6.8×10^{-6} M). [b] Fluorescence quantum yield (±10%) in dichloromethane determined relative to quinine sulfate in 0.1 M H_2SO_4 as standard ($\Phi_F = 0.54$).[21] [c] Excitation at 382 nm. [d] Excitation at 330 nm. [e] Excitation at 350 nm. [f] Calculated using the fluorescence maxima at 393 nm.

observation might be related to the poor luminescent properties of ferrocene derivatives.[19]

A red shift of the absorption and emission bands, along with an increase in the value of the fluorescence quantum yield (Φ_F), was observed on increasing electron-donating strength of the aromatic groups. Phenyl derivatives **2a**−**e** and naphthyl derivatives **2k**,**l** provide good examples of this trend. The calculated HOMO−LUMO energy gaps are in good agreement with the experimental values obtained from the UV/vis spectra (see Supporting Information, Table S1).

Compounds **3a**,**b** (with one biphenyl unit per arm) have higher values of λ_{abs}, λ_{em}, and ε than analogous compounds **2a**,**b** (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 compound **3a**, whereas compound **3b** had a lower Φ_F value, probably due to more effective aggregation.

A similar bathochromic tendency is observed on changing from phenyl rings[9d] to naphthyl (**2j**,**k**) and then anthracyl (**2m**) or phenanthryl (**2n**) derivatives. Comparison of compound **3a** with **4** reveals that the replacement of a benzene by a thiophene ring in each arm of the oligomer causes a red shift of the absorption and the emission as well as a decrease in ε and Φ_F.

Surprisingly, thienyl compounds **2g** and **2i** have low fluorescence, whereas similar molecules without vinyl bridges are highly emissive.[9b] This finding might be related to the low luminescence of oligothienylenevinylene.[20]

The UV/vis spectra for compounds **6** and **8** consist of a simple superposition of the absorptions due to the independent chromophores. As one would expect, the absorption becomes much stronger in dendritic compound **8a** owing to the exponential increase in the number of light-absorbing phenylenevinylene units.

In general, large Stokes shifts occur. This phenomenon is particularly noteworthy in dendritic compound **8a**, where a Stokes shift up to 10 344 cm^{-1} is observed. The magnitudes of the Stokes shifts indicate large (vibrational, electronic, geometric) differences between the excited state reached immediately after absorption and the excited state from which the emission starts. Charge-transfer processes should be fairly effective due to the presence of a π-donor and a π-acceptor group (pyrimidine)

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TABLE 3. Optical Properties of Several Divinylpyrimidines in Different Solvents

	hexane ($\Delta f = -0.001$)[b]		THF ($\Delta f = 0.209$)[b]		CH_2Cl_2 ($\Delta f = 0.217$)[b]		methanol ($\Delta f = 0.308$)[b]	
compd[a]	λ_{abs}max	λ_{em}max	λ_{abs}max	λ_{em}max	λ_{abs}max	λ_{em}max	λ_{abs}max	λ_{em}max
2a	296, 359, 377	388, 409	366	430	296, 369	444	297, 373	489
2c	298, 408, 426	444, 467	419	517	301, 427	540	298, 428	583
2f	315, 394, 416	431, 451	318, 406	485	289, 408	496	318, 420	531
2l	275, 338, 361	397, 425, 451	262, 282, 377	450	263, 283, 380	470	262, 283, 374	519
8a	328	410, 430	330	491	330	508	325	407

[a] All spectra were recorded at room temperature at $c = 2$ mg/L (1.8×10^{-6} to 6.8×10^{-6} M). [b] Solvent orientation polarizabilities (Δf).[23]

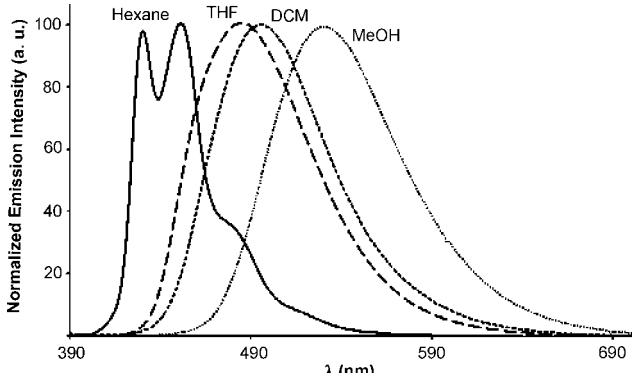

FIGURE 1. Normalized emission of compound **2f** in various solvents ($c = 2$ mg/L).

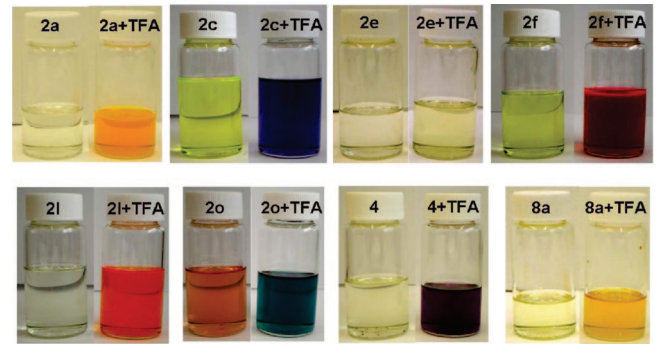

FIGURE 2. Changes in color of CH_2Cl_2 solutions of several vinylpyrimidines ($c = 2$ mg/L) in the presence of 10^{-2}M TFA.

directly connected by the phenylenevinylene system. This effect also leads to a very low degree of self-absorption of emitted light. Hence, these compounds are expected to perform well in organic light-emitting diodes and as laser dyes.

In an effort to gain further insight into the photophysical process within these V-shaped molecules, we investigated the absorption and emission behaviors of **2a**, **2c**, **2f**, **2l**, and **8a** in different solvents. The results of these investigations are summarized in Table 3. The absorption spectra are nearly independent of solvent polarity, except for a slight, insignificant red shift that indicates a negligible intramolecular interaction between donor and acceptor groups in the ground state. In contrast, the emission spectra exhibit distinct solvent dependence. Broad structureless emission and larger Stokes shifts were observed on increasing the solvent polarity along with a successive decrease in the fluorescence intensity. This solvatochromic behavior, which results from the stabilization of the highly polar emitting state by polar solvents, is typical for compounds that undergo an internal charge transfer upon excitation and has been fully documented for numerous fluorophores containing donor−acceptor units.[22] As an example, the PL spectra for compound **2f** are shown in Figure 1. Interestingly, the emission of dendritic compound **8a** appears again narrow and strongly blue-shifted in methanol, with a maximum wavelength of 407 nm. Whereas in THF and CH_2Cl_2 the charge-separated state can be formed with energy transfer from the peripheral phenylenevinylene chromophores, in methanol the energy transfer should not take place. Thus, emission is only obtained from the peripheral phenylenevinylene units with a complete quenching of the fluorescence of the pyrimidine moiety in this polar protic solvent. This quenching can be attributed to the hydrogen bond interaction between the molecule and surrounding solvent, which results in an additional nonradiative decay. Indeed, two bands at 424 and 532 nm can be observed in a nonprotic polar solvent such as DMSO ($\Delta f = 0.263$), where only a partial energy transfer from the phenylenevinylene units should occur (see Supporting Information for PL spectra of **2a**, **2c**, **2l**, and **8a**).

The nitrogen atoms of all the prepared pyrimidines are basic centers that can be protonated. Thus, the effect of protonation on the optical properties of CH_2Cl_2 solutions of vinylpyrimidines **2a**, **2c**, **2e**, **2f**, **2l**, **2o**, **4**, and **8a** was also studied. Dichloromethane solutions of these compounds underwent a significant color change in the presence of TFA (10^{-2} M), with the exception of **2e** (Figure 2). This color change was found to be fully reversible by neutralization with a base such as Et_3N or KBu^tO.

The change in the UV−vis absorption spectra of **2a** upon addition of acid is illustrated in Figure 3. The spectra show the progressive attenuation of the absorption band for the neutral compound on increasing the concentration of TFA from 10^{-5} to 10^{-2} M, whereas a new, more intense red-shifted band corresponding to the protonated species appeared (see Supporting Information for spectra of the other compounds described here).

As far as the emission properties are concerned, the protonated forms of compounds **2a**, **2f**, **2e**, **2l**, and **4** remain emissive with a red-shifted fluorescence (Table 4 and Figure 4). In contrast, pyrimidine **2c** becomes nonemissive upon addition of TFA. In this case, not only the pyrimidine ring but also the diphenylamino group can be protonated, and therefore, the

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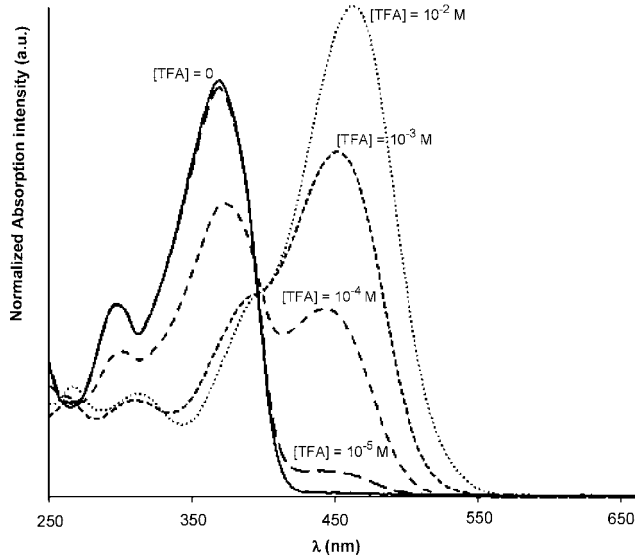

FIGURE 3. UV/vis absorption changes of **2a** in CH_2Cl_2 ($c = 2$ mg/L) with increasing TFA concentration.

TABLE 4. UV/Vis and PL Data for Several Prepared Divinylpyrimidines upon Addition of TFA

compd[a]	UV/vis (TFA 10^{-2} M in CH_2Cl_2) λ_{max}, nm (ε, M^{-1} cm^{-1})	PL (CH_2Cl_2) λ_{max}, nm	Φ_F	Stokes shifts cm^{-1}
2a	462 (42000)	546	0.33[b]	2164
2c	297 (24100), 581 (54300)			
2e	380 (31200)	445	0.06[c]	3844
2f	538 (61200)	596	0.17[c]	1809
2l	315 (15000), 482 (39600)	590	0.19[b]	2075
2o	407 (26000), 629 (12400)			
4	354 (27000), 553 (255900)	666	0.03[b]	1808
8a	331 (86000), 409 (29800)			

[a] All spectra were recorded at room temperature at $c = 2$ mg/L (1.8×10^{-6} to 6.8×10^{-6} M). [b] Fluorescence quantum yield (±10%) in dichloromethane determined relative to fluorescein in 0.1 M NaOH as standard ($\Phi_F = 0.79$).[24] [c] Fluorescence quantum yield (±10%) in dichloromethane determined relative to quinine sulfate in 0.1 M H_2SO_4 as standard ($\Phi_F = 0.54$),[21] excitation at 382 nm.

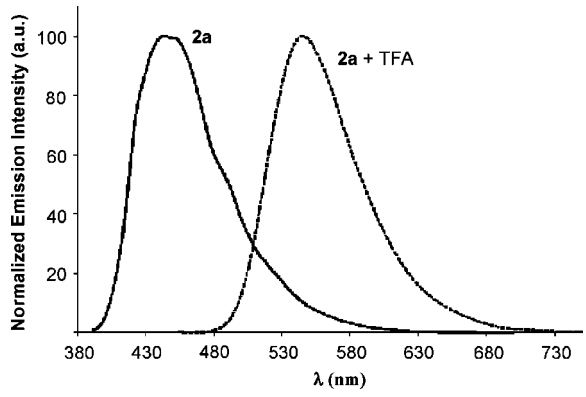

FIGURE 4. Normalized PL spectra of **2a** in CH_2Cl_2 ($c = 2$ mg/L) with and without addition of TFA.

ability of the latter to donate electrons is significantly attenuated. Ferrocenyl derivative **2o** remains nonemissive after protonation.

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Conclusions

In conclusion, we have successfully synthesized and characterized a series of new 4,6-bis(arylvinyl)pyrimidines in a straightforward manner by aldol condensation between 4,6-dimethylpyrimidine and the appropriate aromatic aldehyde. The protocol permits not only the preparation of dendritic derivatives but also the stepwise incorporation of different aldehydes, resulting in molecules that are functionalized in an asymmetric fashion. The *meta*-substitution pattern causes all chromophores to be independent, and all of the compounds present absorption wavelengths in the UV or visible region, emitting light with large Stokes shifts. The materials exhibit strong emission solvatochromism, and red-shifted broad structureless bands are obtained in polar solvents, an observation characteristic of intramolecular charge transfer at excited states. The pH sensing properties of these compounds were also studied. These compounds display a dramatic and reversible color change and luminescence switching upon addition of acid as a result of the protonation of the nitrogen atoms of the pyrimidine ring. These findings suggest that suitable design of the molecules and a sound understanding of their spectroscopic properties could enable promising colorimetric and luminescence pH sensors to be developed.

Experimental Section

General Procedure for the Dicondensation of Aldehydes and 4,6-Dimethylpyrimidine. Preparation of Compounds 2 and 8.[9d] A stirred mixture of 4,6-dimethylpyrimidine **1** (108 mg, 1.0 mmol) and the corresponding aldehyde (2.0 mmol) in aqueous sodium hydroxide (5 M, 15 mL) containing Aliquat 336 (43 mg, 0.1 mmol) was heated under reflux for 1 h (1 M NaOH and 8 h under reflux was used for compound **2e**). The mixture was allowed to cool, and the precipitate was filtered off, washed with water, and purified by recrystallization from the indicated solvent. Representative examples are described below.

(*E*,*E*)-4,6-Bis(4-hexyloxystyryl)pyrimidine (2a): Colorless solid; yield 81%; mp 126.9−128.3 °C (EtOH); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.91 (t, 6H, $J = 7.0$ Hz), 1.33−1.37 (m, 8H), 1.47 (m, 4H), 1.80 (m, 4H), 3.99 (t, 4H, $J = 7.0$ Hz), 6.92 (A of AB_q, 4H, $J = 8.5$ Hz), 6.93 (A of AB_q, 2H, $J = 16.0$ Hz), 7.21 (d, 1H, $J = 1.0$ Hz), 7.54 (B of AB_q, 4H, $J = 8.5$ Hz), 7.85 (B of AB_q, 2H, $J = 16.0$ Hz), 9.05 (d, 1H, $J = 1.0$ Hz); ^{13}C NMR and DEPT ($CDCl_3$, 125 MHz) δ 14.0 (CH_3), 22.6 (CH_2), 25.7 (CH_2), 29.2 (CH_2), 31.6 (CH_2), 68.1 (CH_2), 114.9 (CH), 115.8 (CH), 123.4 (CH), 128.3 (C), 129.1 (CH), 136.6 (CH), 158.6 (CH), 160.3 (C), 162.9 (C). Anal. Calcd for $C_{32}H_{40}N_2O_2$: C, 79.30; H, 8.32; N, 5.78. Found; C, 78.99; H, 8.15; N, 5.74.

(*E*,*E*,*E*,*E*,*E*)-4,6-Bis[3,5-bis(4-hexyloxystyryl)styryl]pyrimidine (8a): Pale yellow solid; yield 70%; mp 136.2−138.3 °C ($CHCl_3$/EtOH); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.92 (t, 12H, $J = 7.0$ Hz), 1.33−1.38 (m, 16H), 1.48 (m, 8H), 1.80 (m, 8H), 3.99 (t, 8H, $J = 7.0$ Hz), 6.91 (A of AB_q, 8H, $J = 8.5$ Hz), 6.99 (A of AB_q, 4H, $J = 16.0$ Hz), 7.14 (A of AB_q and B of AB_q, 6H, $J = 16.0$ Hz), 7.35 (d, 1H, $J = 1.0$ Hz), 7.47 (B of AB_q, 8H, $J = 8.5$ Hz), 7.57 (br s, 2H), 7.58 (s, 4H), 7.92 (B of AB_q, 2H, $J = 16.0$ Hz), 9.13 (d, 1H, $J = 1.0$ Hz); ^{13}C NMR and DEPT ($CDCl_3$, 125 MHz) δ 14.1 (CH_3), 22.6 (CH_2), 25.7 (CH_2), 29.2 (CH_2), 31.6 (CH_2), 68.1 (CH_2), 114.7 (CH), 116.3 (CH), 124.2 (CH), 125.1 (CH), 125.7 (CH), 126.1 (CH), 127.8 (CH), 129.2 (CH), 129.6 (C), 136.3 (C), 137.0 (CH), 138.6 (CH), 158.7 (CH), 159.0 (C), 162.7 (C); MS (FAB+, *m*-NBA) *m*/*z* 1093.3 ($MH^{+\bullet}$); HRMS *m*/*z* calcd for $C_{76}H_{89}N_2O_4$ 1093.6822, found 1093.6841.

General Procedure for the Monocondensation of Aldehydes and 4,6-Dimethylpyrimidine. Preparation of Compounds 5. To a stirred solution of 4,6-dimethylpyrimidine **1** (108 mg, 1.0 mmol)

and KBu^{t}O (1 mmol) in refluxing THF (30 mL) under argon was added a solution of the corresponding aldehyde (1.0 mmol) in THF (30 mL) in four portions every 15 min. The mixture was heated for 1 h. The mixture was allowed to cool, water was added, and the THF was evaporated under vacuum. For **5a**, the mixture was extracted with EtAcO (×3), dried ($MgSO_4$), and the solvent evaporated. For **5b**, the solid was filtered off, washed with water, and purified. A representative example is described below.

(*E*)-4-(4-Hexyloxystyryl)-6-methylpyrimidine (5a). Purification by column chromatography (Al_2O_3, hexanes/EtAcO, 7:3) gave the title compound as a colorless solid: yield 32%; mp 77−78 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.91 (t, 3H, J = 7.0 Hz), 1.32−1.37 (m, 4H), 1.47 (m, 2H), 1.79 (m, 2H), 2.52 (s, 3H), 3.99 (t, 2H, J = 7.0 Hz), 6.87 (A of AB_q, 1H, J = 16.0 Hz), 6.91 (A of AB_q, 2H, J = 9.0 Hz), 7.14 (s, 1H), 7.53 (B of AB_q, 2H, J = 9.0 Hz), 7.82 (B of AB_q, 1H, J = 16.0 Hz), 9.00 (d, 1H, J = 1.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.0, 22.6, 24.2, 25.7, 29.2, 31.6, 68.2, 114.9, 123.2, 128.2, 129.1, 136.7, 158.4, 160.3, 162.4, 167.1. Anal. Calcd for $C_{19}H_{24}N_2O$: C, 76.99; H, 8.16; N, 9.45. Found: C, 77.12; H, 8.14; N, 9.37.

General Procedure for the Preparation of Asymmetric Compounds 6. All operations were identical to those described for the synthesis of compounds **2** and **8**, except that monocondensation products **5** were used as the starting materials. A representative example is described below.

(*E*,*E*)-4-(4-Trifluoromethylstyryl)-6-(4-dimethylaminostyryl)pyrimidine (6c): Orange solid; purified by column chromatography (Al_2O_3, hexanes/EtAcO, 7:3); mp 205−207 °C; yield 68%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.03 (s, 6H), 6.72 (A of AB_q, 2H, J = 8.5 Hz), 6.87 (A of AB_q, 1H, J = 16.0 Hz), 7.12 (A of AB_q, 1H, J = 16.0 Hz), 7.25 (s, 1H), 7.52 (B of AB_q, 2H, J = 8.5 Hz), 7.65 (A of AB_q, 2H, J = 8.5 Hz), 7.70 (B of AB_q, 2H, J = 8.5 Hz), 7.86 (B of AB_q, 1H, J = 16.0 Hz), 7.91 (B of AB_q, 1H, J = 16.0 Hz), 9.06 (s, 1H); ^{13}C NMR and DEPT ($CDCl_3$, 125 MHz) δ 40.2 (NCH_3), 112.1 (CH), 116.2 (CH), 120.5 (CH), 123.5 (C), 124.0 (q, J = 270.2 Hz, CF_3), 125.8 (q, J = 3.9 Hz, CH), 127.6 (CH), 128.5 (CH), 129.3 (CH), 130.7 (q, J = 32.6 Hz, C), 134.7 (CH), 138.0 (CH), 139.3 (C), 151.3 (C), 158.6 (CH), 161.4 (C), 164.1 (C).

General Procedure for Suzuki Cross-Coupling Reactions. Preparation of Compounds 3 and 4. A stirred mixture of bromo derivative (1 mmol), arylboronic acid (2.5 mmol), $Pd(PPh_3)_4$ (0.1 mmol), aqueous 2 M potassium carbonate (2.5 mmol, 1.25 mL), and ethanol (1.5 mL) in degassed toluene (20 mL) was heated under reflux under nitrogen for 40 h. The reaction mixture was cooled, and the precipitate was filtered off. A representative example is described below.

(*E*,*E*)-4,6-Bis[4-(4-dimethylaminophenyl)styryl]pyrimidine (3b): Brown-gray solid; yield 80%; mp >260 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.02 (s, 12H), 6.81 (A of AB_q, 4H, J = 8.5 Hz), 7.09 (A of AB_q, 2H, J = 16.0 Hz), 7.31 (s, 1H), 7.56 (B of AB_q, 4H, J = 8.5 Hz), 7.62 (A of AB_q, 4H, J = 8.5 Hz), 7.65 (B of AB_q, 4H, J = 8.5 Hz), 7.93 (B of AB_q, 2H, J = 16.0 Hz), 9.10 (s, 1H); ^{13}C NMR and DEPT ($CDCl_3$, 125 MHz) δ 40.5 (CH_3), 112.7 (CH), 116.2 (CH), 124.9 (CH), 126.4 (CH), 127.6 (CH), 128.0 (C), 128.2 (CH), 133.4 (C), 136.8 (CH), 142.2 (C), 150.2 (C), 158.7 (CH), 162.9 (C). MS (CI+, isobutane) m/z 523 (MH^+). Anal. Calcd for $C_{36}H_{34}N_4$: C, 82.72; H, 6.56; N, 10.72. Found: C, 82.49; H, 6.41; N, 10.48.

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Supporting Information Available: Characterization data and copies of ^{1}H NMR and ^{13}C NMR spectra for all compounds; calculated and experimental HOMO−LUMO energy gaps for compounds **2**; emission spectra for **2a**, **2c**, **2l**, and **8a** in various solvents; absorption spectra of **2c**, **2e**, **2f**, **2l**, **2o**, and **8a** with increasing TFA concentration; and emission spectra of **2f** and **2l** with and without addition of TFA. This material is available free of charge via the Internet at http://pubs.acs.org.

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