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4-Arylvinyl-2,6-di(pyridin-2-yl)pyrimidines: Synthesis and Optical Properties

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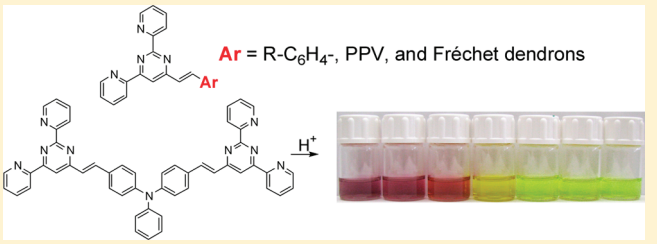
Supporting Information

ABSTRACT: A series of 4-arylvinyl-2,6-di(pyridin-2-yl)-pyrimidines have been efficiently prepared by a double cross-coupling reaction between 2,4-dichloro-6-methylpyrimidine and 2-(tributylstannyl)pyridine, followed by aldol condensation with the appropriate aromatic aldehyde substituted with electron-donating, electron-withdrawing, dendritic, or water-soluble groups. The effect of different protic and aprotic solvents on the optical absorption and emission properties of these systems was studied. Compounds with electron-donating groups display strong emission solvatochromism, suggesting the formation of an intramolecular charge-separated emitting state. The solvatochromic behavior depends not only on the solvent polarity but also on the hydrogen bonding parameters of the solvent. The effect of protonation was also studied, and the abilities of some of these molecules to function as colorimetric and luminescent pH sensors were demonstrated with dramatic color changes and luminescence switching upon the introduction of acid.



INTRODUCTION

Over the past decade, there has been considerable interest in the synthesis and characterization of conjugated organic compounds due to their applications in a wide range of electronic and optoelectronic devices. Indeed, such compounds are used as liquid crystals,[1] components for light-emitting devices (OLEDs) for displays and lighting,[2] as field effect transistors (OFETs),[3] and in single molecular electronics.[4] Fluorescent chromophores, which are generally known to have planar and rigid π-conjugated systems, are also of interest as functional materials in molecular probes.[5] Molecular fluorescence enables high sensitivity in detection, "ON−OFF" switchability, subnanometer spatial resolution, and submillisecond temporal resolution.[6]

Since the late 1990s, fluorescent oligopyridines have been of considerable interest as tunable fluorophores through intermolecular interactions. The parent oligopyridines (2,2′-bipyridine, 2,2′:6′,2″-terpyridine, and 1,10-phenanthroline) possess extremely low fluorescence quantum yields and undesirable short emission wavelengths. However, the introduction of electron-donating moieties leads to an enhancement in quantum yields and a shift to the visible region of the emission wavelength.[7] 2,2′:6′,2″-Terpyridine is well-known for its good coordination ability due to its suitably arranged ring nitrogens. Among the unique properties of terpyridines, their luminescent properties upon coordination with metal ions are particularly attractive due to the high potential for technological applications such as light-emitting devices and probes over a large spectral range.[8] The assembly of these useful materials is based on the large binding constants between the terpyridine ligand and various metal ions. To date, many complexes have been investigated, and it has been widely demonstrated that the choice of ligand has a marked influence on the luminescence properties of the resulting supramolecular assemblies.[9]

More recently, pyrimidine has also been used in the above context. Thus, conjugated 2,4,6-trisubstituted pyrimidine derivatives have shown important fluorescence properties,[10] as well as self-assembly properties,[10e,11] and 2,4-diarylvinylpyrimidines have also been described as good fluorophores,[12] pH sensors,[13] and two-photon absorption chromophores.[14] Functionalization of pyrimidine with two 2-pyridyl groups in positions 2 and 4 leads to an effective tridentate ligand for metal cations (similar to a 2,2′:6′,2″-terpyridine) that can generate various useful materials. For example, a dinuclear ruthenium complex with this ligand was described as a near IR-emitting Ru(II) complex that exhibits the longest-lived emission and highest quantum yield reported to date.[15] The additional nitrogen of the pyrimidine ring is responsible for a less efficient nonradiative pathway, thus providing a flat bridging acceptor ligand that can lead to a large delocalized π surface. Therefore, the synthesis of new pyrimidine analogues of terpyridine is a good option to obtain high emission efficiency as well as new emission colors.

Dendrons are monodisperse wedge-shaped dendrimer sections with multiple terminal groups and a single reactive function at the focal point.[16] Among their unique properties,[17] it has been demonstrated that dendritic arms can function as light harvesting antennae.[18] Conjugated dendrimers with poly(phenylenevinylene) (PPV) and poly(phenyleneethynylene) scaffolds[19] and poly(benzyl ether) dendrimers (also called Fréchet-type dendrimers)[20] represent two important groups within this class of

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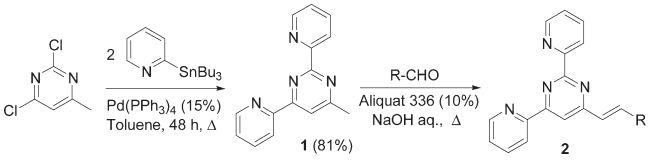
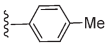
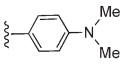
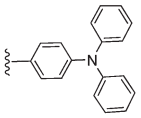
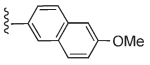
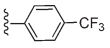
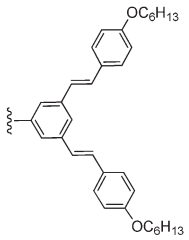
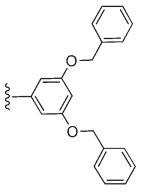
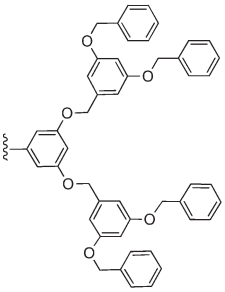
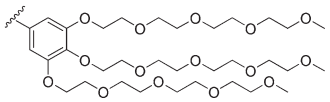
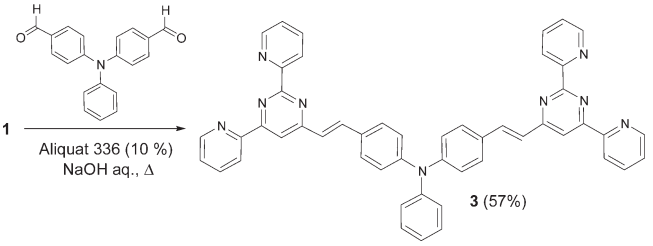
Table 1. Preparation of Di(pyridin-2-yl)pyrimidines



Compd	R	Isolated yield (%)
2a		73
2b		64
2c		53
2d		60
2e		53
2f		41
2g		55
2h		65
2i		48
2j		33

materials. Terpyridine ligands have been successfully attached to the focal point of phenylacetylene dendrons.[21] Such binding-ligand anchored dendrons exhibited broad absorption, large molar extinction coefficients, and high fluorescence quantum yields. However, di(pyridin-2-yl)pyrimidine derivatives bearing artificial light-harvesting dendritic systems with a cascade-type energy gradient have not been investigated in detail.

Scheme 1. Synthesis of the A−π−D−π−A Compound 3



In this contribution, we describe the synthesis and characterization of a novel series of fluorescent 2,6-di(pyridin-2-yl)-pyrimidines functionalized with phenylenevinylene arms bearing either electron-donating or electron-withdrawing groups. These highly conjugated molecules have an A−π−D or A−π−A structure (A = acceptor, D = donor) because of the strong electron-withdrawing character of the 2,6-di(pyridin-2-yl)-pyrimidine unit. 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 Fréchet and PPV dendritic structures on the di(pyridin-2-yl)pyrimidine unit was also assessed in an effort to combine the properties of both types of chromophores.

Additionally, the potential behavior of the 2,6-di(pyridin-2-yl)pyrimidine moiety as a ligand can also be used to modulate the optoelectronic properties of these molecules. An in-depth study into the complexation of these compounds with various metal cations will be published elsewhere.

RESULTS AND DISCUSSION

Preparation of 2,6-Di(pyridin-2-yl)pyrimidines. The target compounds **2a**−**j** were prepared in two steps from commercially available 2,4-dichloro-6-methylpyrimidine (Table 1). The first step was a double cross-coupling reaction with 2-(tributylstannyl)pyridine under Stille conditions.[22] The second step involved the aldol condensation between aromatic aldehydes and the methylpyrimidine derivative **1** in boiling aqueous 5 M NaOH (1 M for **2f**) using Aliquat 336 as a phase-transfer catalyst in the absence of an organic solvent.[23] The experimental protocol is straightforward and offers easy access, in moderate to good yields, to a wide variety of di(pyridin-2-yl)pyrimidines containing electron-withdrawing and -donating groups, as well as PPV and Fréchet-type dendrons.

A similar protocol gave the A−π−D−π−A derivative **3**, which contains two push−pull systems, in moderate yield (57%) after a double condensation reaction between 4,4′-diformyltriphenylamine and the methylpyrimidine drivative **1** (Scheme 1).

All new compounds were soluble in THF, chloroform, and dichloromethane (**2j** was also soluble in water) and were characterized using a variety of analytical techniques. The overall purities of these products 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

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Table 2. UV/vis and Photoluminescence (PL) Data

compd[a]	UV/vis λ_{max}, nm (ε, $M^{-1}\cdot cm^{-1}$)	PL λ_{max}, nm	Φ_F	Stokes shift, cm^{-1}
2a	283 (31400), 335 (24600)	407	<0.01[b]	5281
2b	283 (32400), 339 (31000)	484	<0.01[b]	9215
2c	278 (22400), 413 (21300)	540	0.22[c]	5695
2d	282 (31000), 416 (31300)	540	0.52[c]	5520
2e	280 (41600), 357 (35900), 369 (36100)	461	0.15[c]	5455
2f	281 (31300), 331 (20300)	423	<0.01[b]	6571
2g	293 (57000), 332 (79900)	505	0.05[b]	10319
2h	282 (26300), 338 (22200)	430	0.02[b]	6329
2i	281 (31900), 339 (21500)	425	0.02[b]	6056
2j	279 (15400), 355 (16800)	494	0.22[c]	7867
3	280 (48000), 439 (37100)	544	0.46[d]	4387

[a] All spectra were recorded in CH_2Cl_2 solutions at room temperature at $c = 1.0 \times 10^{-5}$ M to 3.0×10^{-5} M for UV/vis spectra and 1.0×10^{-6} to 3.0×10^{-6} M for PL spectra. [b] Fluorescence quantum yield (±10%) determined relative to quinine sulfate in 0.1 M H_2SO_4 as standard ($\Phi_F = 0.54$); excitation at 340 nm. [c] Fluorescence quantum yield (±10%) determined relative to anthracene in ethanol as standard ($\Phi_F = 0.27$); excitation at 356 nm. [d] Fluorescence quantum yield (±10%) determined relative to rhodamine 101 in ethanol as standard ($\Phi_F = 0.92$); excitation at 526 nm.

unequivocally established on the basis of the coupling constant for the vinylic protons in the ^{1}H NMR spectra ($J \sim 16$ Hz).

These materials are perfectly stable in the solid state and could be stored without the need for any special precautions. Only compound **2j** underwent partial *cis*−*trans* isomerization when it was allowed to stand in chloroform solution at room temperature.

UV/vis and PL Spectroscopy. The optical properties of the prepared structures were investigated by UV/vis and photoluminescence (PL) spectroscopy in CH_2Cl_2 solutions at room temperature and at low concentration (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). Under these conditions, aggregation or self-absorption effects were not observed. The data obtained are summarized in Table 2. All compounds were photostable and did not undergo *cis*−*trans* isomerization under the analysis conditions. As an example, the spectra for derivatives **2g** and **3** are shown in Figure 1.

The UV/vis spectra showed strong absorption bands at λ_{max} = 331−439 nm, and these were accompanied in all cases by a second or even a third band at higher energy. The materials are also fluorescent and emit light when irradiated, showing a typical response in the visible region (407−544 nm). In comparison with di(pyridin-2-yl)pyrimidine **2a** (model compound), derivatives **2b**−**e** exhibited red-shifted absorption and fluorescence emission spectra that are consistent with an increase in the electron-donating character of the substituent in the aromatic ring. In contrast, compound **2f**, which contains an electron-withdrawing group (R = *p*-CF_3−C_6H_4−), showed a lower energy absorption band and a small red-shift in the emission band. The introduction of electron-donating groups also led to an increase in the value of the fluorescence quantum yield (Φ_F). The A−π−D−π−A derivative **3** has a higher λ_{abs} value, a similar λ_{ems} value, and a lower quantum yield than the analogous A−π−D compound **2d**.

As far as the dendritic materials are concerned, the UV/vis spectra of compounds **2g**−**i** consist of a simple superposition of the absorptions due to the independent chromophores. The spectra exhibited insignificant red shifts in the absorption bands, indicating a negligible intramolecular interaction between the donor dendritic wedges and the acceptor arylvinyl-2,6-di(pyridin-2-yl)pyrimidine unit in the ground state. On the other hand, when compounds **2h** and **2i** were excited in the dendron absorption band at 282 and 281 nm, respectively, the fluorescence of the benzyl ether dendrons ($\lambda_{max} \sim 345$ nm) was totally quenched, and this was accompanied by an increase in the fluorescence intensity of the arylvinyl-2,6-di(pyridin-2-yl)-pyrimidine moiety (λ_{max} = 430 and 425 nm, respectively). These results show that an efficient energy transfer from the Fréchet-type dendrons to the arylvinyl-2,6-di(pyridin-2-yl)pyrimidine unit takes place. Analogously, excitation of compound **2g** also led to quenching of the fluorescence of the dendritic wedge ($\lambda_{max} \sim 410$ nm). In this case, a band at a maximum wavelength of 505 nm was observed in the spectrum. The ability of both PPV and Fréchet-type dendrons to act as extremely efficient light-harvesting antennae that are capable of transferring light energy has been well documented.[18]

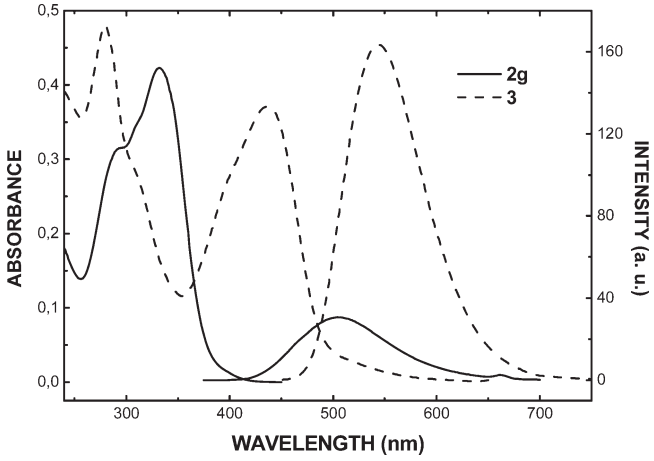

Figure 1. UV/vis and emission spectra of compounds **2g** and **3**.

In general, larges Stokes shifts were obtained for the compounds under investigation. As observed in related structures,[13] this phenomenon is especially relevant for dendritic compound **2g** and indicates large differences (vibrational, electronic, geometric) between the Franck−Condon state and the excited state.

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Table 3. Optical Properties of 2,6-Di(pyridin-2-yl)pyrimidines 2b−d, 2f, and 2g in Various Aprotic Solvents

	n-hexane		THF		CH_2Cl_2		DMSO	
	$\Delta E_T(30)^a$ = 0.0		$\Delta E_T(30)$ = 27.2		$\Delta E_T(30)$ = 42.7		$\Delta E_T(30)$ = 59.0	
	UV/vis	PL	UV/vis	PL	UV/vis	PL	UV/vis	PL
compd	λ_{max}, nm	λ_{max}, nm	λ_{max}, nm	λ_{max}, nm	λ_{max}, nm	λ_{max}, nm	λ_{max}, nm	λ_{max}, nm
2b	281, 339	410, 432	281, 341	445	283, 339	484	285, 346	506
2c	276, 395	435, 458	280, 409	531	278, 413	540	278, 422	598
2d	279, 399	441, 463	281, 411	517	282, 416	540	283, 418	575
2f	279, 328	433	281, 331	421	281, 331	423	283, 334	423
2g	285, 329	412, 428	291, 331	480	293, 332	505	291, 334	553

[a] Dimroth−Reichardt polarity parameter, J·mol^{-1}.

The optical properties of the water-soluble derivative **2j** were also measured in water and compared to those obtained in CH_2Cl_2. Whereas changes were not observed in the absorbance spectrum (λ_{abs} = 280 and 355 nm), a red-shifted emission band (λ_{em} = 535 nm) that led to a high Stokes shift (9650 cm^{-1}) was obtained, and this was accompanied by a decrease in the value of the fluorescence quantum yield (Φ_F < 0.01).

Solvatochromic Behavior. We investigated the absorbance and emission behaviors of di(pyridin-2-yl)pyrimidines **2b−d**, **2f**, and the dendritic derivative **2g** in different aprotic solvents (*n*-hexane, THF, CH_2Cl_2, and DMSO). The corresponding spectroscopic data are collected in Table 3. The slight, irrelevant changes observed in the absorption spectra again reveal an insignificant intramolecular interaction between donor and acceptor groups in the ground state. In contrast, the emission spectra exhibit distinct solvent dependence. Broad structureless emissions and larger Stokes shifts were observed on increasing the solvent polarity along with a decrease in the fluorescence intensity (see Supporting Information, Figures S1−S5). The correlation of the emission maxima with the solvent-dependent $\Delta E_T(30)$ Dimroth−Reichardt polarity parameter is represented in Figure 2 and was found to be positively linear for di(pyridin-2-yl)pyrimidines **2b−d** and **2g**. This is typical solvatochromic behavior for compounds that undergo an internal charge transfer upon excitation, leading to a highly polar, charge-separated emitting state stabilized by polar solvents.[13,24] Indeed, the presence of strong electron-donating substituents such as dimethylamine (**2c**) or diphenylamine (**2d**) gave rise to larger slopes (Figure 2) compared to moderate electron-donating substituents (**2b** or **2g**), indicating a stronger influence of the solvent polarity. As expected, compound **2f**, which contains an electron-withdrawing group, did not show a red-shift in either absorbance or emission because formation of the charge transfer state was unfeasible.

Nevertheless, when methanol was used as solvent, the results could not be explained on the basis of the solvent polarity, suggesting that hydrogen bonding may play an important role. Consequently, the solvatochromic behavior of compounds **2b**, **2d**, and **2g** was also studied in polar, protic solvents such as 2-propanol, ethanol, and methanol (Table 4). Similar UV/vis spectra were obtained for these compounds on increasing the polarity and the hydrogen bonding values of the solvents (see Supporting Information, Figures S6−S8). The absorption spectra are also comparable with those obtained in aprotic solvents. Thus, polar solvents do not seem to induce significant changes in the ground state. The lack of correlation of the emission maxima with the solvent polarity can be explained by the presence of a good hydrogen bond acceptor (the pyrimidine ring). The excited states are definitely changed by hydrogen bonding interactions and become more energetic. A solvent-induced red-shift of the

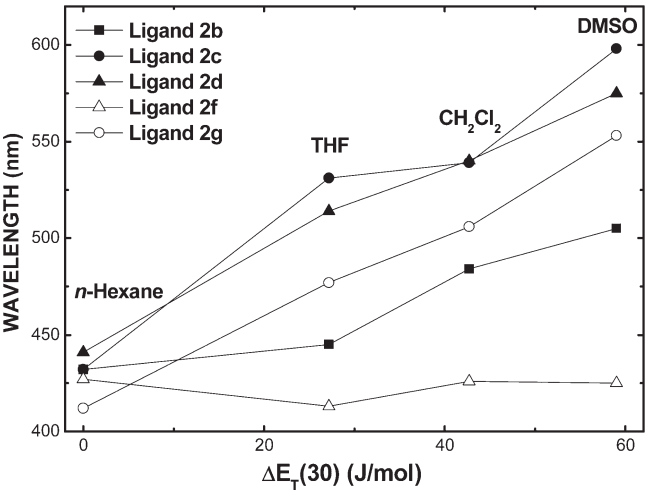

Figure 2. Emission wavelength (λ_{max}) as a function of Dimroth−Reichardt polarity parameter for compounds **2b−d**, **2f**, and **2g**.

Table 4. Optical Properties of 2,6-Di(pyridin-2-yl)pyrimidines 2b, 2d, and 2h in Polar, Protic Solvents

	2-propanol		ethanol		methanol	
	$\Delta E_T(30)^a$ = 82.8		$\Delta E_T(30)$ = 87.9		$\Delta E_T(30)$ = 103.0	
	α^b = 0.76		α = 0.86		α = 0.98	
	UV/vis	PL	UV/vis	PL	UV/vis	PL
compd	λ_{max}, nm	λ_{max}, nm	λ_{max}, nm	λ_{max}, nm	λ_{max}, nm	λ_{max}, nm
2b	284, 341	415	284, 342	425	284, 342	431
2d	282, 416	557	283, 417	574	283, 416	590
2g	291, 327	535	327	440, 550	327	410

[a] Dimroth−Reichardt polarity parameter, J·mol^{-1}. [b] Hydrogen bonding parameter.

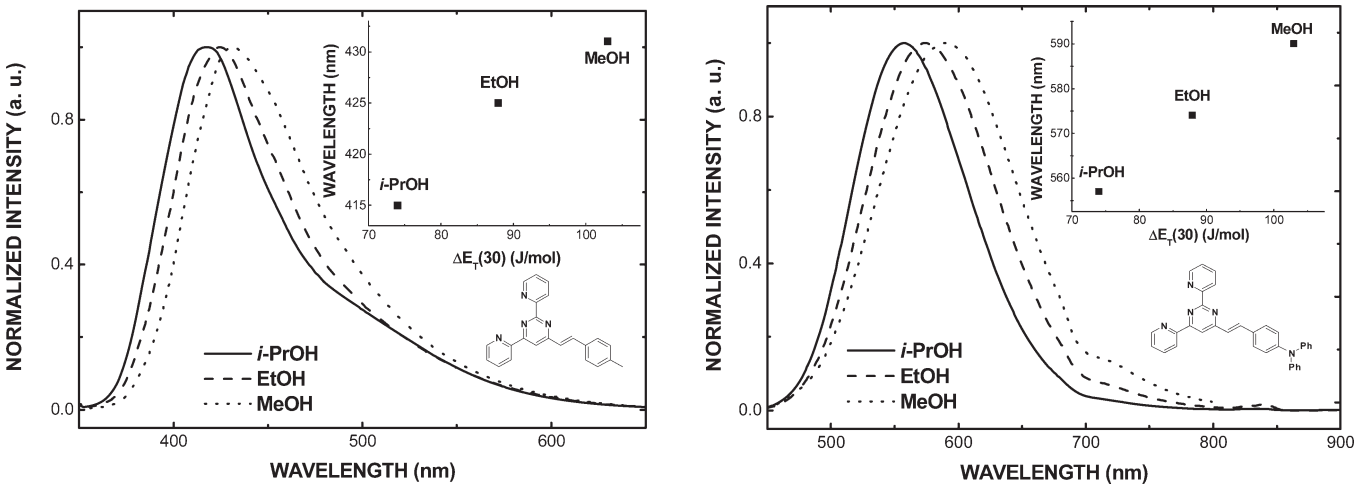

Figure 3. Normalized emission spectra of **2b** (left) and **2d** (right) in protic solvents. Inset: wavelength as a function of Dimroth−Reichardt polarity parameter. For a UV−vis version, see Supporting Information, Figures S6 and S7.

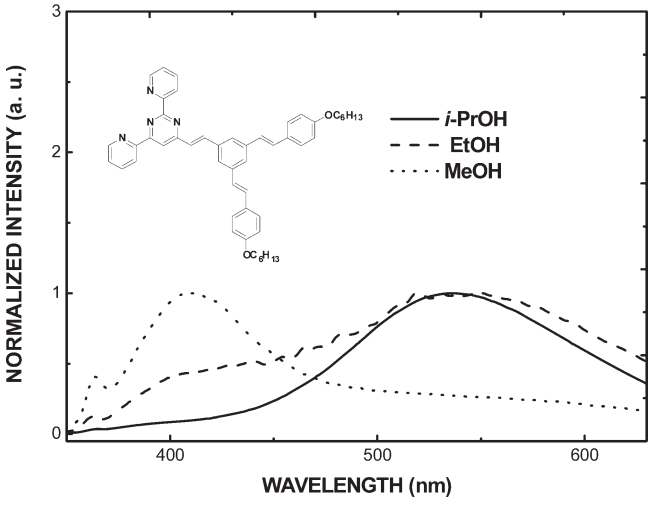

Figure 4. Normalized emission spectra of **2g** in protic solvents. For a UV−vis version, see Supporting Information Figure S8.

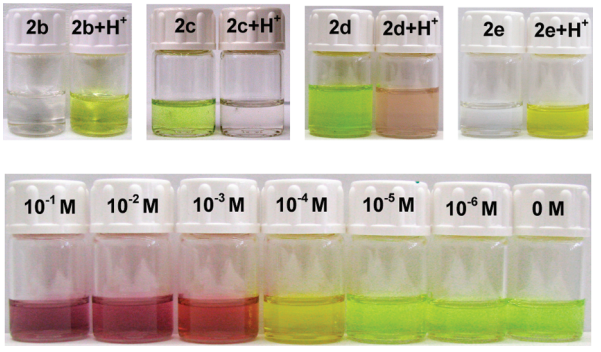

Figure 5. Top: Change in color of THF solutions of several di(pyridin-2-yl)pyrimidines ($c = 6.3 \times 10^{-6}$ to 1.3×10^{-5} M) in the presence of 10^{-2} M *p*-TSA. Bottom: Change in color of THF solutions of **3** with increasing *p*-TSA concentration.

emission maxima was found for derivatives **2b** and **2d** on increasing the polarity, once again suggesting the formation of a charge transfer emitting state (Figure 3). The positive linear correlation between the emission maxima and the $\Delta E_T(30)$ Dimroth−Reichardt polarity parameter indicates that the effect of hydrogen bonding is comparable for all alcoholic solvents. In contrast, this effect is not comparable for all alcohols in the dendritic compound **2g**. In this case, the emission maximum was totally dependent on the hydrogen bonding parameter: i.e., as the hydrogen bonding ability increased, the excited state also increased in energy (see Figure 4).

Protonation Studies. In a previous study,[13] we demonstrated the ability of related 4,6-bis(arylvinyl)pyrimidines to function as colorimetric and luminescent pH sensors due to the basic character of the nitrogen atoms of the pyrimidine ring. From this point of view, we decided to evaluate the effect of protonation on the optical properties of several of the prepared di(pyridin-2-yl)pyrimidines (**2b**−**e** and **3**). In an analogous way to their bis(arylvinyl)pyrimidine counterparts, THF solutions of compounds **2b**−**e** underwent significant color changes in the presence of *p*-TSA (*para*-toluenesulfonic acid, 10^{-2} M) (Figure 5). This color change was found to be fully reversible by neutralization with a base such as Et_3N.

The changes in the UV−vis spectra of **2b** upon addition of acid are illustrated in Figure 6. 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. This is a general behavior except for di(pyridin-2-yl)pyrimidine **2c** (Table 5, see Supporting Information for spectra of the other compounds), for which a blue-shifted band could be observed—probably due to the protonation of the more strongly basic dimethylamino group.

As far as the PL spectra are concerned, only compounds **2b** and **2e** remained slightly emissive after protonation, and these showed a red-shifted fluorescence (Table 5 and Figure 6). In contrast, di(pyridin-2-yl)pyrimidines **2c**−**d** and **3** became nonemissive upon addition of *p*-TSA. In these cases, not only the pyrimidine ring but also the dimethyl and diphenylamino groups can be protonated, and therefore their ability to donate electrons is significantly attenuated.

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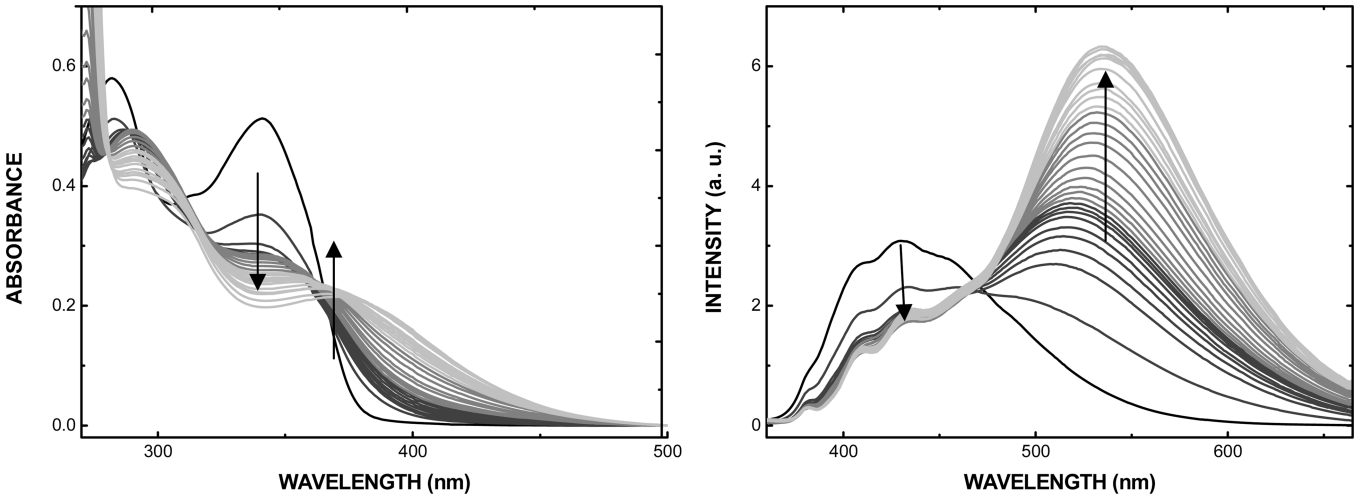

Figure 6. Changes in the absorption (left) and emission (right) spectra of **2b** (2.0×10^{-5} M in THF) upon addition of *p*-TSA (7.5×10^{-5} M to a large excess).

Table 5. Optical Properties of Di(pyridin-2-yl)pyrimidines 2b−e and 3g upon Addition of *p*-TSA

	UV/vis (*p*-TSA 10^{-2} M in THF)	PL (THF)	Stokes shift
compd[a]	λ_{max}, nm (ε, $M^{-1}.cm^{-1}$)	λ_{max}, nm	cm^{-1}
2b	372 (14700)	542	8432
2c	359 (13100)	--[b]	--
2d	297 (34800), 470 (19000)	--[b]	--
2e	420 (16100)	540	5291
3	303 (33800), 521 (23700)	--[b]	--

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

CONCLUSIONS

In summary, a new series of 2,6-di(pyridin-2-yl)pyrimidines functionalized with phenylenevinylene groups at the 4-position has been efficiently prepared by a straightforward two-step synthetic methodology. The protocol permits not only the incorporation of electron-donating and electron-withdrawing groups at the end of the π-conjugated system but also functionalization with water-soluble groups and dendritic wedges. The resulting compounds were characterized using a variety of techniques. The optical properties were studied and were found to be comparable to those of the bis(arylvinyl)pyrimidine counterparts previously reported by us.[13] Thus, all of the molecules present absorption wavelengths in the UV or visible region and emit light with significant Stokes shifts. The results of solvatochromism studies support the formation of very polar excited intramolecular charge transfer states with terminal electron-donating groups. Likewise, these 4-arylvinyl-2,6-di(pyridin-2-yl)pyrimidines display a dramatic and reversible color change and luminescence switching upon addition of acid. This phenomenon is due to the protonation of the nitrogen atoms of the pyrimidine ring. This behavior indicates that this type of material is also valuable for the development of colorimetric and luminescent pH sensors. Nevertheless, in contrast to bis(arylvinyl)pyrimidines, the presence of the 2,6-di(pyridin-2-yl)pyrimidine moiety enables the coordination of different families of metal cations. An in-depth study into the ability of these molecules to act as binding ligands, in an effort to tune their optoelectronic properties, will be reported elsewhere.

EXPERIMENTAL SECTION

General. In air- and moisture-sensitive reactions, all glassware was flame-dried and cooled under Ar. NMR spectra were acquired at 25 °C. Chemical shifts are given in parts per million relative to TMS (^{1}H, 0.0 ppm), $CDCl_3$ (^{13}C, 77.0 ppm), and $CFCl_3$ (^{19}F, 0.0 ppm). IR spectra were recorded on an FT-IR spectrophotometer equipped with an ATR accessory. UV/vis and fluorescence spectra were recorded using standard 1 cm quartz cells. Compounds were excited at their absorption maxima (band of lowest energy) for recording the emission spectra (uncorrected); 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. MALDI-TOF mass spectra were registered in positive reflection mode using dithranol as the matrix material. Melting points are uncorrected. 3,4,5-Tris(2,5,8,11-tetraoxatridecan-13-yloxy)-benzaldehyde, used for the synthesis of **2j**, was prepared according to the literature.[25]

4-Methyl-2,6-di(pyridin-2-yl)pyrimidine (1). A solution of tetrakis(triphenylphosphine)palladium (338 mg, 0.293 mmol), 2-(tributylstannyl)pyridine (90%) (2 g, 4.89 mmol), and 2,4-dichloro-6-methylpyrimidine (318 mg, 1.95 mmol) in toluene (25 mL) was heated under reflux for 48 h under argon. The mixture was allowed to cool, and water (30 mL) was added. The mixture was filtered, and the aqueous phase was extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography (alumina, eluent: hexanes to ethyl acetate) to give 394 mg (81%) of the title compound as a beige solid. Mp 90−92 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.78 (s, 3H), 7.41−7.45 (m, 2H), 7.88−7.92 (m, 2H), 8.26 (s, 1H), 8.66 (d, 1H, J = 8.5 Hz), 8.69 (d, 1H, J = 8.0 Hz), 8.74−8.75 (m, 1H), 8.88−8.90 (m, 1H). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$) δ 24.9 (CH_3), 115.9 (CH), 122.1 (CH), 123.8 (CH), 124.7 (CH), 125.4 (CH), 136.9 (CH), 137.1 (CH), 149.5 (CH), 150.1 (CH), 154.1 (C), 155.2 (C), 162.8 (C), 163.2 (C), 169.5 (C). IR (ATR) ν 1578, 1565, 1466, 1435, 1369, 993, 806, 761 cm^{-1}. MALDI-TOF m/z 248.4 [M^+]. Anal. Calcd for $C_{15}H_{12}N_4$: C, 72.56; H, 4.87; N, 22.57. Found: C, 72.37; H, 4.89; N, 22.43.

(*E*)-2,4-Di(pyridin-2-yl)-6-styrylpyrimidine (2a). Aliquat 336 (20 mg, 0.049 mmol), benzaldehyde (60 mg, 0.570 mmol), 4-methyl-2,6-di(pyridin-2-yl)pyrimidine **1** (118 mg, 0.475 mmol), and aqueous 5 M NaOH (10 mL) were placed in a 50 mL round-bottomed flask. The reaction mixture was heated under reflux with stirring for 6 h. The mixture was allowed to cool and was diluted with water (50 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The residue was purified by column chromatography (alumina, eluent: hexane/ethyl acetate, 3:7) to give 117 mg (73%) of **2a** as a beige solid. Mp 170−171 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35−7.46 (m, 6H), 7.77 (d, 2H, J = 7.5 Hz), 7.92 (dt, 2H, J = 2.0 and 8.0 Hz), 8.04 (d, 1H, J = 16.5 Hz), 8.53 (s, 1H), 8.70 (dt, 1H, J = 1.0 and 8.0 Hz), 8.74 (dt, 1H, J = 1.0 and 8.0 Hz), 8.78 (dq, 1H, J = 1.0 and 4.5 Hz), 8.92 (dq, 1H, J = 1.0 and 5.0 Hz). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$) δ 112.8 (CH), 122.2 (CH), 124.0 (CH), 124.7 (CH), 125.4 (CH), 127.0 (CH), 127.7 (CH), 128.9 (CH), 129.3 (CH), 135.9 (C), 136.8 (CH), 137.1 (CH), 137.5 (CH), 149.4 (CH), 150.1 (CH), 154.2 (C), 155.4 (C), 163.4 (C), 163.5 (C), 165.1 (C). IR (ATR) ν 1639, 1576, 1556, 1523, 1367, 972, 808, 767 cm^{-1}. MALDI-TOF m/z 336.7 [M$^+$]. Anal. Calcd for $C_{22}H_{16}N_4$ (336.14): C, 78.55; H, 4.79; N, 16.66. Found: C, 78.30; H, 4.92; N, 16.36.

(*E*)-4-(4-Methylstyryl)-2,6-di(pyridin-2-yl)pyrimidine (2b). This compound was prepared from Aliquat 336 (46 mg, 0.113 mmol), 4-methylbenzaldehyde (176 mg, 1.47 mmol), and 4-methyl-2,6-di-(pyridin-2-yl)pyrimidine **1** (280 mg, 1.23 mmol) using the same procedure described for **2a**. The reaction mixture was heated under reflux with stirring for 2 h. The residue was purified by crystallization from a mixture of EtAcO/hexanes (10 mL, 1/1) to give 275 mg (64%) of **2b** as a beige solid. Mp 142−144 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.39 (s, 3H), 7.23 (d, 2H, J = 8.0 Hz), 7.38 (d, 1H, J = 16.0 Hz), 7.42−7.46 (m, 2H), 7.57 (d, 2H, J = 8.0 Hz), 7.91 (td, 2H, J = 1.5 and 7.5 Hz), 8.01 (d, 1H, J = 16.0 Hz), 8.51 (s, 1H), 8.70 (dt, 1H, J = 1.0 and 7.5 Hz), 8.73 (dt, 1H, J = 1.0 and 7.5 Hz), 8.77 (br d, 1H, J = 4.5 Hz), 8.91 (br d, 1H, J = 4.5 Hz). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$) δ 21.4 (CH_3), 112.7 (CH), 122.1 (CH), 123.9 (CH), 124.7 (CH), 125.4 (CH), 126.0 (CH), 127.7 (CH), 129.6 (CH), 133.1 (C), 136.9 (CH), 137.1 (CH), 137.5 (CH), 139.6 (C), 149.4 (CH), 150.1 (CH), 154.2 (C), 155.4 (C), 163.4 (C), 163.5 (C), 165.0 (C). IR (ATR) ν 1633, 1577, 1564, 1557, 1520, 1368, 968, 826, 764 cm^{-1}. MALDI-TOF m/z 350.5 [M$^+$]. Anal. Calcd for $C_{23}H_{18}N_4$: C, 78.83; H, 5.18; N, 15.99. Found: C, 78.50; H, 4.92; N, 15.76.

(*E*)-4-(4-Dimethylaminostyryl)-2,6-di(pyridin-2-yl)pyrimidine (2c). This compound was prepared from Aliquat 336 (52 mg, 0.126 mmol), 4-(dimethylamino)benzaldehyde (227 mg, 1.52 mmol), and 4-methyl-2,6-di(pyridin-2-yl)pyrimidine **1** (315 mg, 1.27 mmol) using the same procedure described for **2a**. The reaction mixture was heated under reflux with stirring for 2 h. The residue was washed with a hot ethanol to give 281 mg (58%) of **2c** as a red solid. Mp 182−184 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.04 (s, 6H), 6.74 (d, 2H, J = 9.0 Hz), 7.22 (d, 1H, J = 16.0 Hz), 7.41−7.45 (m, 2H), 7.57 (d, 2H, J = 8.0 Hz), 7.91 (td, 2H, J = 2.0 and 8.0 Hz), 7.98 (d, 1H, J = 16.0 Hz), 8.45 (s, 1H), 8.70 (br d, 1H, J = 8.5 Hz), 8.71 (br d, 1H, J = 8.5 Hz), 8.77 (br d, J = 4.0 Hz, 1H), 8.91 (br d, J = 4.0 Hz, 1H). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$) δ 40.2 (CH_3), 112.0 (CH), 112.1 (CH), 122.1 (CH), 122.3 (CH), 123.9 (CH), 124.0 (C), 124.5 (CH), 125.2 (CH), 129.2 (CH), 136.6 (CH), 137.1 (CH), 138.0 (CH), 149.4 (CH), 150.1 (CH), 151.2 (C), 154.5 (C), 155.6 (C), 162.9 (C), 163.4 (C), 165.7 (C). IR (ATR) ν 1602, 1556, 1508, 1359, 1182, 974, 810, 764, 740 cm^{-1}. MALDI-TOF m/z 380.4 [M + H$^+$]. Anal. Calcd for $C_{24}H_{21}N_5$ (379.18): C, 75.97; H, 5.58; N, 18.46. Found: C, 75.64; H, 5.46; N, 18.17.

(*E*)-4-(4-Diphenylaminostyryl)-2,6-di(pyridin-2-yl)pyrimidine (2d). This compound was prepared from Aliquat 336 (40 mg, 0.098 mmol), 4-(diphenylamino)benzaldehyde (346 mg, 1.27 mmol), and 4-methyl-2,6-di(pyridin-2-yl)pyrimidine **1** (242 mg, 0.975 mmol) using the same procedure described for **2a**. The reaction mixture was heated under reflux with stirring for 2 h. The residue was purified by column chromatography (alumina, eluent: hexane/ethyl acetate, 1:1) to give 295 mg (60%) of **2d** as a yellow solid. Mp 181−182 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04−7.11 (m, 4H), 7.12−7.18 (m, 4H), 7.27−7.34 (m, 5H), 7.40−7.46 (m, 2H), 7.52 (d, 2H, J = 8.5 Hz), 7.91 (td, 2H, J = 2.0 and 8.0 Hz), 7.99 (d, 1H, J = 16.0 Hz), 8.49 (s, 1H), 8.69 (br d, 1H, J = 8.0 Hz), 8.73 (br d, 1H, J = 8.0 Hz), 8.76 (br d, 1H, J = 4.5 Hz), 8.91 (br d, 1H, J = 4.5 Hz). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$) δ 112.4 (CH), 122.1 (CH), 122.2 (CH), 123.7 (CH), 123.9 (CH), 124.6 (CH), 124.7 (CH), 125.2 (CH), 125.3 (CH), 128.7 (CH), 129.2 (C), 129.4 (CH), 136.8 (CH), 137.0 (CH), 137.1 (CH), 147.1 (C), 149.0 (C), 149.4 (CH), 150.1 (CH), 154.3 (C), 155.5 (C), 163.2 (C), 163.5 (C), 165.2 (C). IR (ATR) ν 1627, 1575, 1562, 1519, 1487, 1469, 1369, 1269, 748 cm^{-1}. MALDI-TOF m/z 504.5 [M + H$^+$]. Anal. Calcd for $C_{34}H_{25}N_5$ (503.21): C, 81.09; H, 5.00; N, 13.91. Found: C, 80.99; H, 5.26; N, 14.07.

(*E*)-4-[2-(6-Methoxynaphthalen-2-yl)vinyl]-2,6-di(pyridin-2-yl)pyrimidine (2e). This compound was prepared from Aliquat 336 (26 mg, 0.064 mmol), 6-methoxy-2-naphthaldehyde (122 mg, 0.650 mmol), and 4-methyl-2,6-di(pyridin-2-yl)pyrimidine **1** (162 mg, 0.652 mmol) using the same procedure described for **2a**. The reaction mixture was heated under reflux with stirring for 6 h. The residue was washed with ethanol to give 143 mg (52%) of **2e** as a yellow solid. Mp 185−187 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.95 (s, 3H), 7.15−7.20 (m, 2H), 7.42−7.46 (m, 3H), 7.61−7.83 (m, 3H), 7.85−8.10 (m, 3H), 8.20 (d, 1H, J = 16.5 Hz), 8.56 (s, 1H), 8.73 (d, 1H, J = 8.0 Hz), 8.77 (d, 1H, J = 8.0 Hz), 8.79 (br d, 1H, J = 4.5 Hz), 8.95 (br d, 1H, J = 4.0 Hz). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$) δ 55.4 (CH_3), 106.0 (CH), 112.9 (CH), 119.3 (CH), 122.2 (CH), 124.0 (CH), 124.3 (CH), 124.8 (CH), 125.5 (CH), 126.1 (CH), 127.5 (CH), 128.9 (C), 129.0 (CH), 130.0 (CH), 131.3 (C), 135.2 (C), 137.1 (CH), 137.2 (CH), 137.8 (CH), 149.4 (CH), 149.9 (CH), 154.2 (C), 155.2 (C), 158.5 (C), 163.3 (C), 163.5 (C), 165.0 (C). IR (ATR) ν 1622, 1575, 1556, 1519, 1467, 1371, 1259, 1174, 848, 780, 740, 675, 663 cm^{-1}. MALDI-TOF m/z 415.8 [M$^+$]. Anal. Calcd for $C_{27}H_{20}N_4O$ (416.47): C, 77.87; H, 4.84; N, 13.45. Found: C, 77.56; H, 4.72; N, 13.34.

(*E*)-2,4-Di(pyridin-2-yl)-6-(4-trifluoromethylstyryl)pyrimidine (2f). This compound was prepared from Aliquat 336 (16 mg, 0.039 mmol), 4-(trifluoromethyl)benzaldehyde (102 mg, 0.586 mmol), 4-methyl-2,6-di-(pyridin-2-yl)pyrimidine **1** (97 mg, 0.391 mmol), and an aqueous solution of sodium hydroxide (1 M, 15 mL) using the same procedure described for **2a**. The reaction mixture was heated under reflux with stirring for 20 h. The residue was purified by column chromatography (alumina, eluent: hexane/ethyl acetate, 1:1) to give 65 mg (41%) of **2f** as a pale yellow solid. Mp 96−98 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45−7.47 (m, 2H), 7.47 (d, 1H, J = 16.5 Hz), 7.67 (d, 2H, J = 8.0 Hz), 7.76 (d, 2H, J = 8.0 Hz), 7.92−7.94 (m, 2H), 8.07 (d, 1H, J = 16.5 Hz), 8.54 (s, 1H), 8.71 (dd, 1H, J = 1.0 and 8.0 Hz), 8.75 (dd, 1H, J = 1.0 and 8.0 Hz), 8.77 (br d, 1H, J = 4.5 Hz), 8.93 (br d, 1H, J = 4.0 Hz). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$) δ 113.3 (CH), 122.2 (CH), 124.0 (q, J = 270.2 Hz, CF_3), 124.0 (CH), 124.9 (CH), 125.6 (CH), 125.8 (q, J = 3.7 Hz, CH), 127.7 (CH), 129.2 (CH), 130.7 (q, J = 32.6 Hz, C), 135.7 (CH), 137.0 (CH), 137.2 (CH), 139.2 (C), 149.5 (CH), 150.1 (CH), 153.9 (C), 155.0 (C), 163.5 (C), 163.9 (C), 164.1 (C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −63.1. IR (ATR) ν 1555, 1369, 1379, 1163, 1109, 1065, 763 cm^{-1}. MALDI-TOF m/z 403.8 [M$^+$]. Anal. Calcd for $C_{23}H_{15}F_3N_4$ (404.12): C, 68.31; H, 3.74; N, 13.85. Found: C, 68.01; H, 3.83; N, 13.50.

(*E,E,E*)-4-{3,5-Bis[4-(hexyloxy)styryl]styryl}-2,6-di(pyridin-2-yl)-pyrimidine (2g). This compound was prepared from Aliquat 336 (12 mg, 0.029 mmol), 3,5-bis[4-(hexyloxy)styryl]benzaldehyde (165 mg, 0.323 mmol), and 4-methyl-2,6-di(pyridin-2-yl)pyrimidine **1** (73 mg, 0.294 mmol) using the same procedure described above for **2a**. The residue was dissolved in hot ethyl acetate and precipitated with cold ethanol to give 120 mg (55%) of **2g** as a yellow solid. Mp 80−82 °C. ^{1}H NMR (500 MHz,

$CDCl_3$) δ 0.88−0.85 (m, 6H), 1.32−1.40 (m, 8H), 1.45−1.53 (m, 4H), 1.81 (m, 4H), 4.00 (t, 4H, J = 7.5 Hz), 6.93 (d, 4H, J = 8.5 Hz), 7.02 (d, 2H, J = 16.0 Hz), 7.17 (d, 2H, J = 16.0 Hz), 7.42−7.46 (m, 2H), 7.48−7.55 (m, 5H), 7.57 (s, 1H), 7.68 (s, 2H), 7.92 (dt, 2H, J = 1.0 and 7.5 Hz), 8.04 (d, 1H, J = 16.0 Hz), 8.59 (s, 1H), 8.72 (d, 1H, J = 8.0 Hz), 8.74 (d, 1H, J = 8.0 Hz), 8.79 (br d, 1H, J = 5.0 Hz), 8.94 (br d, 1H, J = 5.0 Hz). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$) 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), 112.7 (CH), 114.8 (CH), 122.2 (CH), 124.0 (CH), 124.1 (CH), 124.7 (CH), 125.3 (CH), 125.4 (CH), 125.7 (CH), 127.5 (CH), 127.8 (CH), 129.2 (CH), 129.7 (C), 136.5 (C), 136.8 (CH), 137.1 (CH), 137.4 (CH), 138.6 (C), 149.5 (CH), 150.2 (CH), 154.2 (C), 155.4 (C), 159.1 (C), 163.6 (C), 164.8 (C). IR (ATR) ν 1633, 1576, 1508, 1369, 1244, 1172, 958 cm^{-1}. MALDI-TOF m/z 741.3 [M + H$^+$]. Anal. Calcd for $C_{50}H_{52}N_4O_2$ (740.41): C, 81.05; H, 7.07; N, 7.56. Found: C, 80.75; H, 6.79; N, 7.34.

(*E*)-4-[3,5-Bis-(benzyloxy)styryl]-2,6-di(pyridin-2-yl)pyrimidine (2h). This compound was prepared from Aliquat 336 (24 mg, 0.059 mmol), 3,5-dibenzyloxybenzaldehyde (187 mg, 0.588 mmol), and 4-methyl-2,6-di(pyridin-2-yl)pyrimidine **1** (146 mg, 0.588 mmol) using the same procedure described for **2a**. The reaction mixture was heated under reflux with stirring for 6 h. The reaction mixture was extracted with CH_2Cl_2 (3 × 20 mL). The residue was washed with a mixture of EtOH/hexanes and then with MeOH to give 210 mg (65%) of **2h** as a white solid. Mp 154−156 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.09 (s, 4H), 6.65 (t, 1H, J = 2.0 Hz), 6.92 (d, 2H, J = 2.0 Hz), 7.36−7.44 (m, 13H), 7.91 (br t, 2H, J = 8.0 Hz), 7.93 (d, 1H, J = 16.0 Hz), 8.52 (s, 1H), 8.70 (d, 1H, J = 8.0 Hz), 8.73 (d, 1H, J = 8.5 Hz), 8.77 (br d, 1H, J = 4.0 Hz), 8.91 (br d, 1H, J = 4.5 Hz). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$) δ 70.1 (CH_2), 103.7 (CH), 106.6 (CH), 112.8 (CH), 122.1 (CH), 124.0 (CH), 124.7 (CH), 125.4 (CH), 127.5 (CH), 127.6 (CH), 128.0 (CH), 128.6 (CH), 136.7 (C), 136.9 (CH), 137.1 (CH), 137.4 (CH), 137.8 (C), 149.4 (CH), 150.1 (CH), 154.1 (C), 155.3 (C), 160.2 (C), 163.5 (C), 163.6 (C), 164.7 (C). IR (ATR) ν 1639, 1591, 1575, 1562, 1519, 1435, 1371, 1160, 1043, 968, 821, 738, 678 cm^{-1}. MALDI-TOF m/z 570.2 [M + Na$^+$]. Anal. Calcd for $C_{36}H_{28}N_4O_2$ (548.63): C, 78.81; H, 5.14; N, 10.21. Found: C, 78.50; H, 4.93; N, 9.99.

(*E*)-4-{3,5-Bis[3,5-bis(benzyloxy)benzyloxy]styryl}-2,6-di(pyridin-2-yl)pyrimidine (2i). This compound was prepared from Aliquat 336 (14 mg, 0.033 mmol), 3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzaldehyde (248 mg, 0.334 mmol), and 4-methyl-2,6-di(pyridin-2-yl)pyrimidine **1** (83 mg, 0.588 mmol) using the same procedure described for **2h**. The residue was washed with a mixture of EtOH/hexanes and then with MeOH to give 148 mg (48%) of **2i** as a white solid. Mp 157−159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.04 (s, 4H), 5.06 (s, 8H), 6.59 (t, 2H, J = 2.5 Hz), 6.62 (t, 1H, J = 2.0 Hz), 6.72 (d, 4H, J = 2.5 Hz), 6.92 (d, 2H, J = 2.0 Hz), 7.28−7.48 (m, 23H), 7.91 (td, 2H, J = 1.5 and 7.5 Hz), 7.98 (d, 1H, J = 16 Hz), 8.54 (s, 1H), 8.74 (br d, 1H, J = 7.5 Hz), 8.76 (br d, 1H, J = 4.0 Hz), 8.81 (br d, 1H, J = 8.0 Hz), 8.96 (br d, 1H, J = 4.5 Hz). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$) δ 70.0 (CH_2), 70.1 (CH_2), 101.7 (CH), 103.7 (CH), 106.3 (CH), 106.8 (CH), 113.2 (CH), 122.4 (CH), 124.1 (CH), 125.0 (CH), 125.5 (CH), 127.5 (CH), 127.6 (CH), 128.0 (CH), 128.6 (CH), 136.8 (C), 137.2 (CH), 137.6 (CH), 137.8 (C), 139.1 (C), 149.4 (CH), 149.5 (CH), 154.0 (C), 154.6 (C), 160.1 (C), 160.2 (C), 162.8 (C), 163.8 (C), 164.7 (C). IR (ATR) ν 1591, 1444, 1371, 1149, 1049, 825, 736, 694 cm^{-1}. MALDI-TOF m/z 973.0 [M$^+$]. Anal. Calcd for $C_{64}H_{52}N_4O_6$ (973.12): C, 78.99; H, 5.39; N, 5.76. Found: C, 78.63; H, 5.31; N, 5.56.

(*E*)-2,4-Di(pyridin-2-yl)-6-[3,4,5-tris(2,5,8,11-tetraoxatridecan-13-yloxy)styryl]pyrimidine (2j). This compound was prepared from Aliquat 336 (17 mg, 0.042 mmol), 3,4,5-tris(2,5,8,11-tetraoxatridecan-13-yloxy)benzaldehyde (0.303 mg, 0.419 mmol), and 4-methyl-2,6-di(pyridin-2-yl)pyrimidine **1** (104 mg, 0.419 mmol) using the same procedure described above for **2a**. The reaction mixture was heated under reflux with stirring for 2 h. The residue was purified by precipitation from a mixture of hexane/ether (10 mL, 1:1) to give 131 mg (33%) of **2j** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.37 (s, 6H), 3.38 (s, 3H), 3.52−3.60 (m, 6H), 3.62−3.70 (m, 24H), 3.73−3.76 (m, 6H), 3.81 (t, 2H, J = 5.5 Hz), 3.89 (t, 4H, J = 5.5 Hz), 4.19−4.25 (m, 6H), 6.92 (s, 2H), 7.30 (d, 1H, J = 16.0 Hz), 7.43−7.46 (m, 2H), 7.89 (d, 1H, J = 16.0 Hz), 7.90−7.94 (m, 2H), 8.53 (s, 1H), 8.71 (d, 1H, J = 8.0 Hz), 8.73 (d, 1H, J = 8.0 Hz), 8.77 (br d, 1H, J = 5.5 Hz), 8.92 (br d, 1H, J = 5.0 Hz). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$) δ 59.0 (CH_3), 68.8 (CH_2), 69.7 (CH_2), 70.5 (CH_2), 70.5 (CH_2), 70.6 (CH_2), 70.6 (CH_2), 70.6 (CH_2), 70.6 (CH_2), 70.7 (CH_2), 70.8 (CH_2), 71.9 (CH_2), 72.4 (CH_2), 107.1 (CH), 112.5 (CH), 122.1 (CH), 124.0 (CH), 124.7 (CH), 125.4 (CH), 126.4 (CH), 131.2 (C), 136.9 (CH), 137.1 (CH), 137.2 (CH), 139.6 (C), 149.4 (CH), 150.1 (CH), 152.8 (C), 154.2 (C), 155.3 (C), 163.4 (C), 163.5 (C), 164.8 (C). IR (ATR) ν 1634, 1576, 1562, 1327, 1246, 1097, 768 cm^{-1}. MALDI-TOF m/z 955.1 [M + H$^+$]. Anal. Calcd for $C_{49}H_{70}N_4O_{15}$: C, 61.62; H, 7.39; N, 5.87. Found: C, 61.32; H, 7.13; N, 5.71.

4-{(*E*)-2-[2,6-Di(pyridin-2-yl)pyrimidin-4-yl]vinyl}-*N*-(4-{(*E*)-2-[2,6-di(pyridin-2-yl)pyrimidin-4-yl]vinyl}phenyl)-*N*-phenylaniline (3). This compound was prepared from Aliquat 336 (12 mg, 0.029 mmol), 4,4′-diformyltriphenylamine (87 mg, 0.288 mmol), and 4-methyl-2,6-di(pyridin-2-yl)pyrimidine **1** (150 mg, 0.604 mmol) using the same procedure described above for **2a** after 14 h under reflux. The residue was washed with ethanol to give 126 mg (57%) of **3** as an orange solid. Mp 184−186 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, 5H, J = 9.0 Hz), 7.20 (d, 2H, J = 8.0 Hz), 7.32 (d, 2H, J = 16.5 Hz), 7.35 (t, 2H, J = 8.5 Hz), 7.44 (m, 4H), 7.57 (d, 4H, J = 9.0 Hz), 7.89−7.95 (m, 4H), 7.99 (d, 2H, J = 16.5 Hz), 8.50 (s, 2H), 8.70 (d, 2H, J = 8.0 Hz), 8.77 (d, 2H, J = 8.0 Hz), 7.77 (br d, 2H, J = 4.5 Hz), 8.92 (br d, 2H, J = 5.0 Hz). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$) δ 112.6 (CH), 122.2 (CH), 123.6 (CH), 1 24.0 (CH), 124.4 (CH), 124.7 (CH), 125.2 (CH), 125.4 (CH), 125.8 (CH), 128.8 (CH), 129.6 (CH), 130.3 (C), 136.9 (CH), 137.1 (CH), 146.6 (C), 148.3 (C), 149.4 (CH), 150.0 (CH), 154.3 (C), 155.4 (C), 163.3 (C), 163.4 (C), 165.1 (C). IR (ATR) ν 1556, 1504, 1367, 1274, 1177, 764 cm^{-1}. MALDI-TOF m/z 784.0 [M + Na$^+$]. Anal. Calcd for $C_{50}H_{35}N_9$: C, 78.82; H, 4.63; N, 16.55. Found: C, 78.53; H, 4.30; N, 16.32.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Copies of ^{1}H NMR and ^{13}C NMR spectra for all compounds and absorption and emission spectra in various solvents and with increasing *p*-TSA concentration. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Tschierske, C. *J. Mater. Chem.* **2001**, *11*, 2647–2671. (b) Tschierske, C. *Annu. Rep. Prog. Chem., Sect. C* **2001**, *97*, 191–267.

(2) (a) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402–428. (b) Mitschke, U.; Bäuerle *J. Mater. Chem.* **2000**, *10*, 1471–1509. (c) Lo, S.-C.; Burn, P. L. *Chem. Rev.* **2007**, *107*, 1097–1116.

(3) (a) Fichou, D. *J. Mater. Chem.* **2000**, *10*, 571–589. (b) Kim, D. H.; Park, Y. D.; Jang, Y.; Yang, H.; Kim, Y. H.; Han, J. I.; Moon, D. G.; Park, S.; Chang, T.; Chang, C.; Joo, M.; Ryu, C. Y.; Cho., K. *Adv. Funct. Mater.* **2005**, *15*, 77–82. (c) Funahashi, M.; Zhang, F.; Tamaoki, N. *Adv. Mater.* **2007**, *19*, 353–358.

(4) (a) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791–804. (b) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537–554. (c) Wang, C.; Batsanov, A. S.; Bryce, M. R.; Sage, I. *Org. Lett.* **2004**, *6*, 2181–2184. (d) Elbing, M.; Ochs, R.; Koentopp, M.; Fisher, M.; von Hänisch, C.; Weigend, F.; Evers, F.; Weber, H. B.; Mayor, M. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 8815–8820.

(5) (a) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515–1566. (b) Callan, J. F.; de Silva, A. P.; Magri, D. C. *Tetrahedron* **2005**, *61*, 8551–8588.

(6) Bryan, A. J.; de Silva, A. P.; de Silva, S. A.; Rupasinghe, R. A. D. D.; Sandanayake, K. R. A. S. *Biosensors* **1989**, *4*, 169–174.

(7) (a) Ajayagosh, A.; Carol, P.; Sreejith, S. *J. Am. Chem. Soc.* **2005**, *127*, 14962–14963. (b) Goodall, W.; Williams, J. A. G. *Chem. Commun.* **2001**, 2514–2515. (c) Loren, J. C.; Siegel, J. S. *Angew. Chem., Int. Ed.* **2001**, *40*, 754–757. (d) Raw, S. A.; Taylow, R. J. K. *Chem. Commun.* **2004**, 508–509. (e) Kozhevnikov, V. N.; Shabunina, O. V.; Kopchuk, D. S.; Ustinova, M. M.; König, B.; Kozhevnikov, D. N. *Tetrahedron* **2008**, *64*, 8963–8973. (f) Han, F.-S.; Higushi, M.; Kurth, D. G. *Tetrahedron* **2008**, *64*, 9108–9116.

(8) For recent reviews: (a) Cooke, M. W.; Hanan, G. S. *Chem. Soc. Rev.* **2007**, *36*, 1466–1476. (b) Constable, E. C. *Chem. Soc. Rev.* **2007**, *36*, 246–253. (c) Kurth, D. G.; Higushi, M. *Soft Mater.* **2006**, *2*, 915–927. (d) Andres, P. R.; Schubert, U. S. *Adv. Mater.* **2004**, *16*, 1043–1068.

(9) See for example: (a) Cooke, M. W.; Hanan, G. S.; Loiseau, F.; Campagna, S.; Watanabe, M.; Tanaka, Y. *J. Am. Chem. Soc.* **2007**, *129*, 10479–10488. (b) Camerel, F.; Ziessel, R.; Donnio, B.; Bourgogne, C.; Guillon, D.; Schmutz, M.; Iacovita, C.; Bucher, J. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2659–2662. (c) Carlsson, C. N.; Kuehl, C. J.; Da-Re, R. E.; Veautier, J. M.; Schelter, E. J.; Milligan, A. E.; Scott, B. L.; Bauer, E. D.; Thompson, J. D.; Morris, D. E.; John, K. D. *J. Am. Chem. Soc.* **2006**, *128*, 7230–7241. (d) Coppo, P.; Duati, M.; Kozhevnikov, V. N.; Hofstraat, J. W.; De Cola, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 1806–1810.

(10) (a) Itami, K.; Yamazaki, D.; Yoshida, J.-i. *J. Am. Chem. Soc.* **2004**, *126*, 15396–15397. (b) Achelle, S.; Ramondenc, Y.; Marsais, F.; Plé, N. *Eur. J. Org. Chem.* **2008**, 3129–3140. (c) Achelle, S.; Ramondenc, Y.; Dupas, G.; Plé, N. *Tetrahedron* **2008**, *64*, 2783–2791. (d) Bagley, M. C.; Lin, Z.; Pope, S. J. A. *Tetrahedron Lett.* **2009**, *50*, 6818–6822. (e) Achelle, S.; Plé, N.; Kreher, D.; Attias, A.-J.; Arfaoui, I.; Charra, F. *Tetrahedron Lett.* **2009**, *50*, 7055–7058.

(11) Lin, Y.-C.; Lai, C. K.; Chang, Y.-C.; Liu, K.-T. *Liq. Cryst.* **2002**, *29*, 237–242.

(12) (a) Pascal, L.; Vanden Eynde, J.-J.; Van Haverbeke, Y.; Dubois, P.; Rant, U.; Zojer, E.; Leising, G.; Lazzaroni, R.; Cornil, J.; Brédas, J.-L. *Synth. Met.* **2001**, *119*, 183–184. (b) Pascal, L.; Vanden Eynde, J.-J.; Van Haverbeke, Y.; Dubois, P.; Michel, A.; Rant, U.; Zojer, E.; Leising, G.; Van Dorn, L. O.; Gruhn, N. E.; R.; Cornil, J.; Brédas, J.-L. *J. Phys. Chem. B* **2002**, *106*, 6442–6450.

(13) Achelle, S.; Nouira, I.; Pfaffinger, B.; Ramondenc, Y.; Plé, N.; Rodríguez-López, J. *J. Org. Chem.* **2009**, *74*, 3711–3717.

(14) (a) Liu, B.; Hu, X.-L.; Liu, J.; Zhao, Y.-D.; Huang, Z.-L. *Tetrahedron Lett.* **2007**, *48*, 5958–5962. (b) Liu, Z.; Chen, T.; Liu, B.; Huang, Z.-L.; Huang, T.; Li, S.; Xu, Y.; Qin, J. *J. Mater. Chem.* **2007**, *17*, 4685–4689. (c) Liu, Z.; Shao, P.; Huang, Z.; Liu, B.; Chen, T.; Qin, J. *Chem. Commun.* **2008**, 2260–2262. (d) Li, L.; Tiçan, Y.-P.; Yang, J.-X.; Sun, P.-P.; Wu, J.-Y.; Zhou, H.-P.; Zhang, S.-Y.; Jin, B.-K.; Xing, X.-J.; Wang, C.-K.; Li, M.; Cheng, G.-H.; Tang, H.-H.; Huang, W.-H.; Tao, X.-T.; Jiang, M.-H. *Chem. Asian J.* **2009**, *4*, 668–680. (e) Akdas-Kilig, H.; Roisnel, T.; Ledoux, I.; Le Bozec, H. *New. J. Chem.* **2009**, *33*, 1470–1473. (f) Li, L.; Tian, Y.; Yang, J.; Sun, P.; Kong, L.; Wu, J.; Zhou, H.; Zhang, S.; Jin, B.; Tao, X.; Jiang, M. *Chem. Commun.* **2010**, *46*, 1673–1675.

(15) Polson, M. I. J.; Loiseau, F.; Campagna, S.; Hanan, G. S. *Chem. Commun.* **2006**, 1301–1303.

(16) (a) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons*; Wiley-VCH: Weinheim, 2001. (b) *Dendrimers and other Dendritic Polymers*; Fréchet, J. M. J., Tomalia, D. A., Eds.; Wiley: Chichester, 2001. (c) Grayson, S. M.; Fréchet, J. M. *Chem. Rev.* **2001**, *101*, 3819–3867.

(17) Astruc, D.; Boisselier, E.; Ornelas, C. *Chem. Rev.* **2010**, *110*, 1857–1959.

(18) (a) Burn, P. L.; Lo, S.-C.; Samuel, I. D. W. *Adv. Mater.* **2007**, *19*, 1675–1688. (b) Lo, S.-C.; Burn, P. L. *Chem. Rev.* **2007**, *107*, 1097–1116. (c) Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2000**, 1701–1710. (d) Stuart, G. M.; Fox, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 4354–4360.

(19) García-Martínez, J. C.; Díez-Barra, E.; Rodríguez-López, J. *Curr. Org. Synth.* **2008**, *5*, 267–290.

(20) (a) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638–7647. (b) Hawker, C. J.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010–1013.

(21) Pan, Y.; Lu, M.; Peng, Z.; Melinger, J. S. *Org. Biomol. Chem.* **2003**, *1*, 4465–4470.

(22) (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508–524. (b) Espinet, P.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 4707–4734.

(23) Vanden Eynde, J. J.; Pascal, L.; Van Haverbeke, Y.; Dubois, P. *Synth. Commun.* **2001**, *31*, 3167–3173.

(24) (a) Katan, C.; Terenziani, F.; Mongin, O.; Werts, M. H. V.; Porrès, L.; Pons, T.; Metz, J.; Tretiak, S.; Blanchard-Desce, M. *J. Phys. Chem. A* **2005**, *109*, 3024–3037. (b) Lartia, R.; Allain, C.; Bordeau, G.; Schmidt, F.; Fiorini-Debuischert, C.; Charra, F.; Teulade-Fichou, M.-P. *J. Org. Chem.* **2008**, *73*, 1732–1744. (c) Achelle, S.; Saettel, N.; Baldeck, P.; Teulade-Fichou, M.-P.; Maillard, P. *J. Porphyrins Phthalocyanines* **2010**, *14*, 877–884. (d) Lincker, F.; Kreher, D.; Attias, A.-J.; Do, J.; Kim, E.; Hapiot, P.; Lemaître, N.; Geffroy, B.; Ulrich, G.; Ziessel, R. *Inorg. Chem.* **2010**, *49*, 3991–4001.

(25) Zheng, Q.; Bonoiu, A.; Ohulchanskyy, T. Y.; He, G. S.; Prasad, P. N. *Mol. Pharmaceutics* **2008**, *5*, 389–398.