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Synthesis and Optical Properties of Cross-Conjugated Bis(dimethylaminophenyl)pyridylvinylene Derivatives

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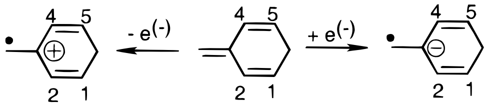
Introduction

The discovery by the Cambridge group that conjugated poly(*p*-phenylenevinylene) (PPV) polymers can be used as promising organic emissive materials in polymer light emitting diodes (PLEDs) in 1990,[1] engendered considerable interest in using organic materials in PLEDs in both academia and industry.[2−9] Their low cost, lightweight, potential ease of fabrication into large areas, high fluorescence quantum yield, color tunability and low turn-on voltage make these the most studied materials. In the recent past, Thompson,[10,11] Swager[12,13] and Ferraris[14,15] have investigated various aspects of poly(pyridinevinylenes). Ferraris showed that a set of 2,6-linked polymers and their corresponding model compounds[14,15] exhibit somewhat unusual photophysical properties. We initiated our studies of the 2,4- and 2,6- linked poly(pyridinevinylenes) to investigate a potential novel conductivity switching mechanism *sui generis* to the pyridine moieties.

We considered an idea for producing a **p-doped polymer without the removal of electrons**, based on an unsaturated polymer whose extended conjugation is blocked by cross-conjugating double bonds. Removal of cross-conjugation by protonation or alkylation of the cross-conjugated sites results in cations with "switched on" conjugation.

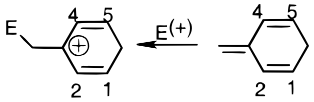
As shown in Scheme 1, carbon atoms 1 and 5 in **D** can be joined in conjugation by the simple stratagem of reduction or oxidation, where the cationic site is an empty p orbital of the 5-carbon π-conjugated array and the anionic site is a filled p orbital of the same π-conjugated array. Indeed, thirteen years ago Swager and Grubbs removed the cross-conjugated nature of a polyacetylene by p-doping.[16]

Scheme 1



D

Scheme 2



Note that **electrophilic attack on the cross-conjugated double bond through protonation or alkylation has the same effect as oxidation; a concept central to this paper** (Schemes 2 and 3).

An example of a manifestation of the notion is shown below, where electrophilic addition to the nitrogen atom of a pyridine unit of a nonconjugated, unsaturated polymer backbone, converts it to a conjugated delocalized poly-cation. We noted with interest that though Barashkov et al.[14,15] prepared, alkylated and examined copolymer **3**; they did not comment on the above possibility of alkylative doping.

In Scheme 3, the lone pair of the pyridine units is actually an sp^2 orbital, orthogonal to the π-system; it is therefore not obvious that alkylation/protonation should induce the expected effect. If $E^{(+)}$ were a proton, then a simple change in pH would induce conjugation. Note that this is NOT the same concept as "protonic acid doping" of emeraldine base, where protonation induces creation of polarons (radical cations, see below).[17,18]

The substitution pattern on the pyridine rings in Scheme 3 is counterintuitive. Based on phenylene systems, the logical substitution pattern should be 1,4 or

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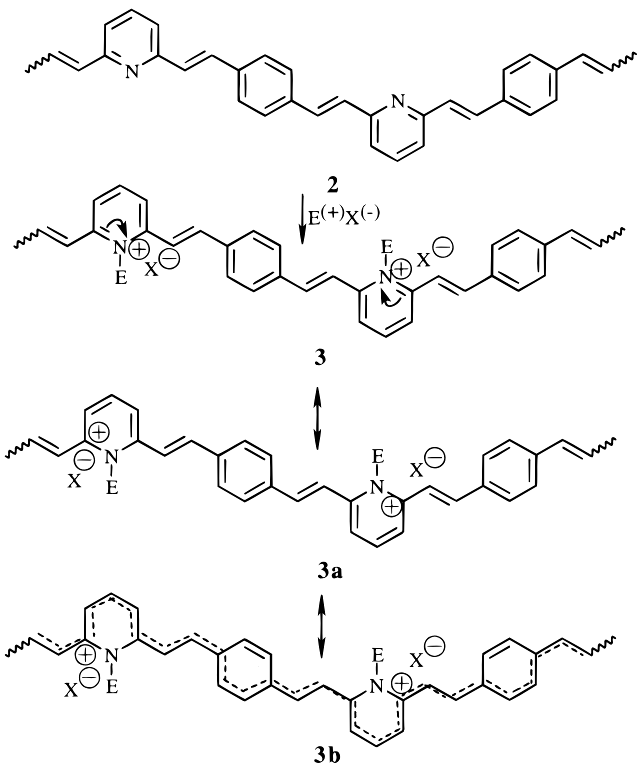
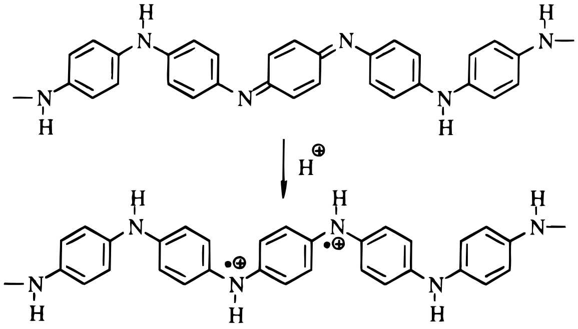
Scheme 3



Scheme 4



1,2 but not 1,3; as discussed here. In this context, interestingly, the authors who studied the poly(2,5-pyridine vinylene) (“1,4-substitution pattern”, **1**, below),[12] do not comment on changes in conductivity upon alkylation of the polymers. There should be no change observed because in that case, the system is already through-conjugated before alkylation.

Actually, the alkylation may be counterproductive if one considers resonance contributor **1Me(b)**, above. Examination of resonance contributor **1Me(a)**, reveals that the “hole” induced by alkylation is decoupled from the through-resonance conjugated backbone by cross-conjugation.

Before launching into the syntheses of the polymers, we prepared model compounds consisting of small oligomers (**I**−**VIII**, Scheme 6), where we purposely placed strong electron donating groups on the para positions of the terminal aromatic rings. The polymers we were going to prepare would have had as terminal units the same dimethylaminophenyl groups. These models were expected to serve the dual purpose of providing a platform to test the concepts outlined above as well as providing significant information for structure determination of the polymers

In the research described here, we have synthesized a series of cross-conjugated (and one conjugated) bis-substituted pyridylvinylene derivatives and studied their absorption and emission properties under different conditions. Solvent, protonation (weak and strong acid) and methylation were investigated.

Experimental Section

Synthesis. The syntheses for the 8 pyridylvinylene derivatives used in this work (Scheme 6) have been reported in the literature.[19−22] Monosubstituted pyridine **I** and **VII** were purchased from Aldrich Chemical Co. and the styrylpyridinium salts **II**,[19] **IV**,[20] **VI**,[21] and **VIII**[22] were prepared according to the literature procedures using the substituted methyl pyridinium *p*-toluenesulfonates and 4-dimethylaminobenzaldehyde in methanol with piperidine as a base. A new synthesis for compound **III** is shown in Scheme 7. Experimental details for the preparation of **III** and **V** using this method are given below.

2,6-Bis(4-dimethylaminostryl)pyridine (III). To a solution of 4.5 g (42 mmol) of 2,6-lutidine in 60 mL of THF was added 65 mL (84.5 mmol) of *sec*-butyllithium (1.3 M in cyclohexane) at −78 °C. After the solution was stirred for 15 min, a solution of 12.6 g (84.5 mmol) of 4-dimethylaminobenzaldehyde in 30 mL of THF was added via syringe over 1 min. The mixture was warmed to 25 °C, stirred 10 h, and poured into 500 mL of 10% aqueous NaCl. Extraction with $CHCl_3$ (3 × 150 mL), drying with $MgSO_4$, and filtration gave a solution of diol. Trifluoroacetic acid (6 mL) was added to the $CHCl_3$ solution followed by refluxing (4 h), cooling to 25 °C and neutralizing to pH 7 with 5% aqueous $NaHCO_3$. The organic layer was dried ($MgSO_4$), concentrated to 30 mL and added to a basic Al_2O_3 column (150 g in $CHCl_3$). Elution of the column with $CHCl_3$ gave 10.9 g (70%) of **III** as a yellow solid after crystallization from methanol: ^1H NMR (400 MHz, $CDCl_3$) δ 2.99 (s, 12 H), 6.73 (d, $J = 9$ Hz, 4 H), 6.98 (d, $J = 16$ Hz, 2 H), 7.13 (d, $J = 8$ Hz, 2 H), 7.50 (d, $J = 9$ Hz, 4 H), 7.51 (t, $J = 9$ Hz, 1 H), and 7.64 (d, $J = 16$ Hz, 2 H); MS (HREI) calcd 369.2205, found 369.2190. Anal. Calcd for $C_{25}H_{27}N_3$: C, 81.26; H, 7.37, N, 11.37. Found: C, 81.16; H, 7.31; N, 11.30.

2,4-Bis(4-dimethylaminostyryl)pyridine (V). Compound **V** was synthesized in 25% yield from 2,4-lutidine using the method described for **III**: ^1H NMR (400 MHz, $CDCl_3$) δ 3.03 (s, 6 H), 3.05 (s, 6 H), 6.72 (d, $J = 5.2$ Hz, 1 H), 6.84 (d, $J = 16.2$ Hz, 1 H), 6.98 (d, $J = 16.3$ Hz, 1 H), 7.15 (d, $J = 5.2$ Hz, 1 H), 7.28 (d, $J = 16.2$ Hz), 7.37 (m, 1 H), 7.47 (m, 4 H), 7.59 (d, $J = 16.2$ Hz, 1 H) and 8.41 (d, $J = 5.3$ Hz, 1 H); MS (EI) 369 (m, 100). Anal. Calcd for $C_{25}H_{27}N_3$: C, 81.26; H, 7.31. Found: C, 81.01; H, 7.09.

Measurements. All solvents used in the spectroscopic study were spectrophotometric grade and were obtained from Aldrich Chemical Co. and J. T. Baker without further purification. Absorption spectra were recorded on a Hewlett-Packard 8453 photodiode array spectrometer and fluorescence spectra were obtained on a SPEX Fluorolog-3 spectrometer. All the spectra were corrected with predetermined instrument response factor. Fluorescence quantum yields were determined by using 9,10-diphenylanthrance as a standard ($\Phi_F = \sim 0.94$ in degassed cyclohexane).[23]

Results and Discussion

UV/Vis Absorption Properties. The absorption spectra of the eight pyridylvinylene derivatives in methanol are shown in Figure 1 and their absorption peak maxima are listed in Table 1. From Scheme 6, Figure 1, and Table 1, several features can be considered. It is clear that the peak maxima of all neutral compounds **I**, **III**, **V**, and **VII**

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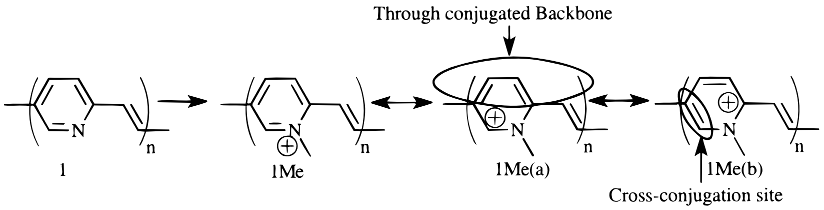
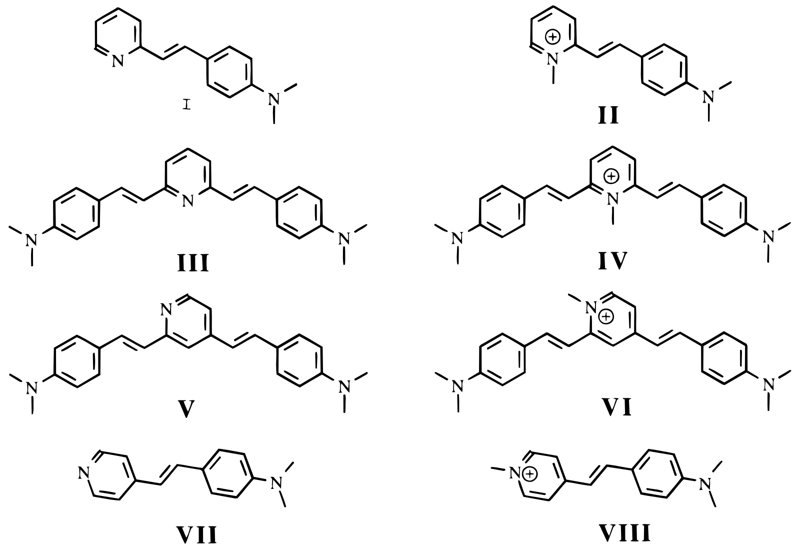
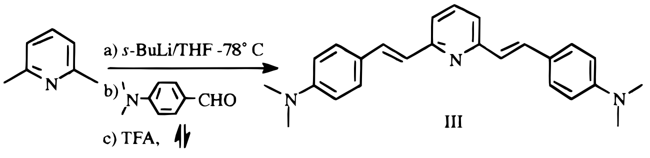
Scheme 5



Scheme 6



Scheme 7



are significantly red shifted after methylation but **III** and **V** show more remarkable shifts The noteworthy absorption red shift upon methylation is consistent with, but more dramatic than, the results of similar pyridylvinylene model compounds reported in the literature.[11,14,15] It is clear from these data that alkylation of the pyridine nitrogen atoms appears to convert this atom to a member of a cyanine array. This interpretation is supported by protonation experiments discussed below. The 4-subsituted pyridylvinylene derivatives have slightly longer conjugation than their corresponding 2-subsituted derivatives (cf. compounds **II** vs **VIII**, or compound **I** vs **VII**).

The effects of solvent on the absorption spectra of the eight compounds are not exceptional. For example, compound **V** shows a minor red shift as solvent polarity increases from hexane to DMSO (Figure 2).

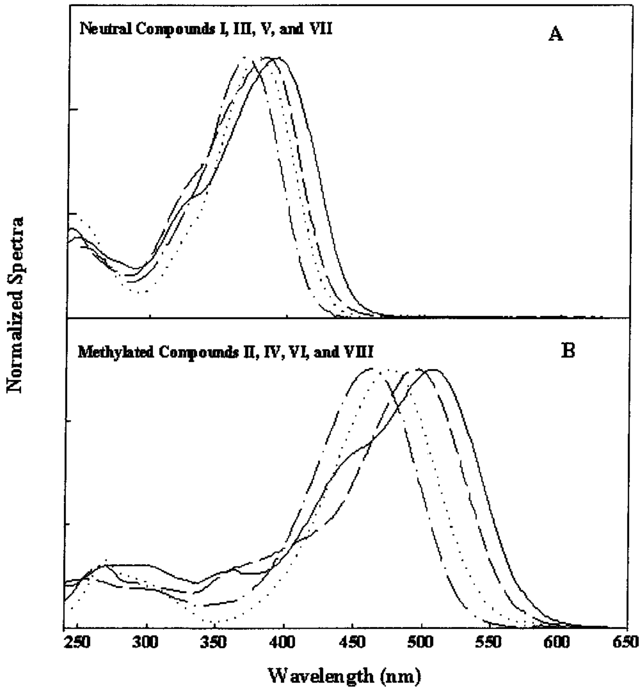


Figure 1. Absorption spectra of pyridylvinylene derivatives in methanol. **A**, neutral compounds **V** (—), **III** (- -), **I** (—•—) and **VII** (•••). **B**, methylated compounds **II** (—•—), **IV** (- -), **VI** (—), and **VIII** (•••).

Emission Properties. The fluorescence spectra of the eight pyridylvinylene compounds were measured in methanol as shown in Figure 3. All the spectra in this polar solvent are broad and structureless, which are similar to those of monosubstituted pyridylvinylene derivatives reported in the literature.[10−15] Their emission peak maxima in methanol are listed in Table 1. All methylated compounds emit at longer wavelength than the corresponding neutral compounds. But, both neutral and methylated compounds are very weakly fluorescent with quantum yields less than 0.01 in methanol. Solvent effects show more dramatic influences on the fluorescence properties, such as spectral shape, spectral position and quantum yield, than their absorption properties. Figure 4 shows the fluorescence spectra of compound **V** in different solvents. As shown, the fluorescence spectra of compound **V** are strongly dependent on the solvent

Table 1. Basic Absorption and Emission Properties of Eight Pyridylvinylene Derivatives in Methanol[a]

compd	ABS (nm)	FLSC (nm)	Φ_F
I	370	482	0.01
II	463	572	0.003
III	384	476	0.004
III triple-H$^{(+)}$	364	423	0.01
IV	495	588	0.0004
V	392	518	0.005
VI	508	645	0.002
V mono-H$^{(+)}$	502	650	0.002
VI double-H$^{(+)}$	342	425	0.007
V triple-H$^{(+)}$	345	425	0.009
VII	378	497	0.01
VIII	476	593	0.003

[a] Quantum yields were determined in methanol by exciting at their absorption peak maxima with 9,10-diphenylanthracene as a standard.

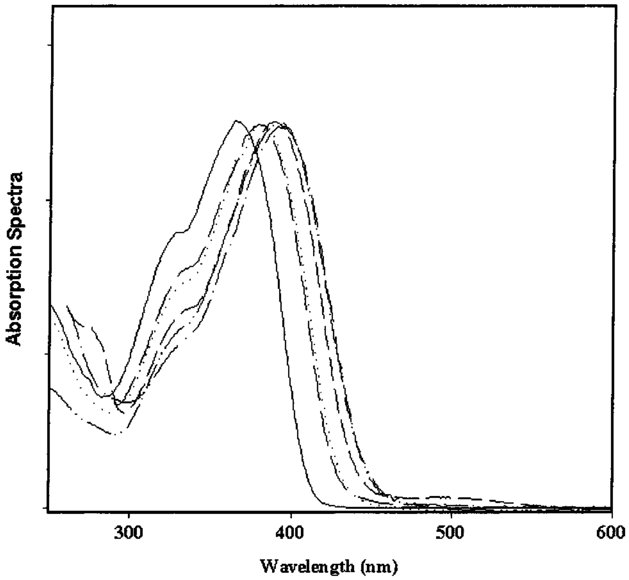


Figure 2. Absorption spectra of compound **V** in solvents hexane (—), toluene (- -), THF (···), MeOH (—··—), DMSO (—·—) and methylene chloride (- — -).

polarity. Somewhat unexpectedly, the fluorescence spectra in solvents of different polarity cover nearly the whole visible region from 400 to 700 nm. Basically, with the exception of methylene chloride or chloroform, the emission spectra shift to the red with increasing solvent polarity. The quantum yields of the eight pyridylvinylene compounds are strongly related to the acidity and polarity of the solvents. For example, the quantum yields of compound **V** in hexane, methanol, and sulfuric acid are 0.22, 0.0050, and 0.10, respectively. In general, the compounds have stronger fluorescence in less polar solvents or under strongly acidic (triple protonation) conditions, detailed in a separate section below.

Protonation Effects. Protonation effects on the electronic absorption and emission properties of the pyridylvinylene derivatives (both neutral and methylated compounds) were examined. It was found that protonation of the pyridylvinylene derivatives can occur either on the nitrogen atoms of pyridine, or pyridine and aniline by adding appropriate amounts of an aqueous HCl solution. For example, in Figure 5A, the absorption spectrum of neutral compound **V** was significantly red-shifted (~110 nm, concomitant color change from yellow to red) upon addition of dilute hydrochloric acid. The new absorptive species has nearly an identical absorption spectrum to that of the corresponding methylated compound **VI** (Figure 5B). The results indicate that protonation of compound **V**, after addition of dilute HCl, occurs on the pyridine nitrogen atom, in accord with the notion that the pyridine nitrogen atom is more basic than the dimethylaniline nitrogen. However, after continued addition of HCl into the red solution of compound **V**, the red color faded and finally disappeared (Figure 5B). Its electronic spectrum (Figure 5A) shows a new blue-shifted peak compared to the absorption spectrum of neutral **V** and, as expected, the absorption peak of the red-shifted species (~500 nm) gradually decreased as the HCl concentration increased. During the addition of increasing amounts of HCl, the spectrum shape remained unchanged with HCl concentration. The most likely scenario is that the new absorptive species is due to the further protonation on the nitrogen atoms of the dim-

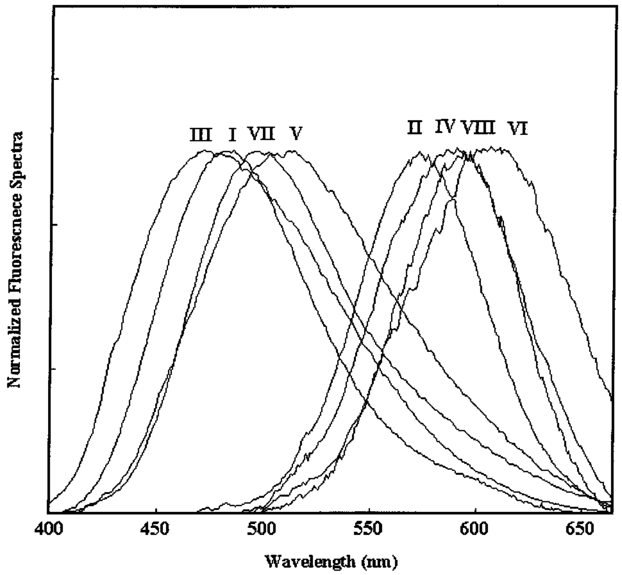


Figure 3. Fluorescence spectra of pyridylvinylene derivatives in methanol.

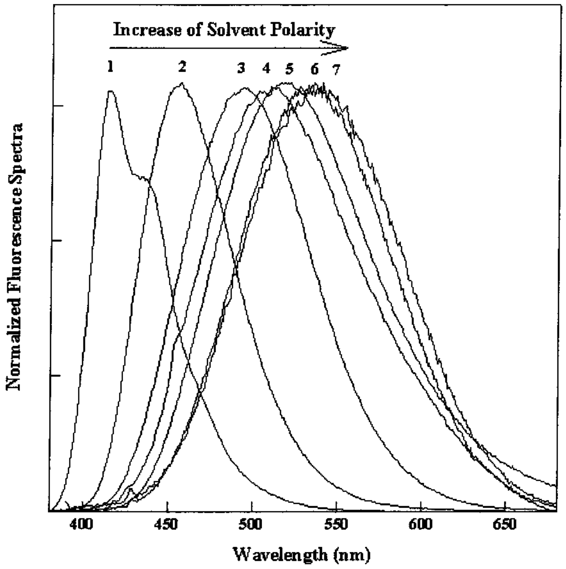


Figure 4. Fluorescence spectra of compound **V** in different solvents: 1, hexane; 2, toluene; 3, THF; 4, MeOH; 5, CH_2Cl_2; 6, MeCN; 7, DMSO.

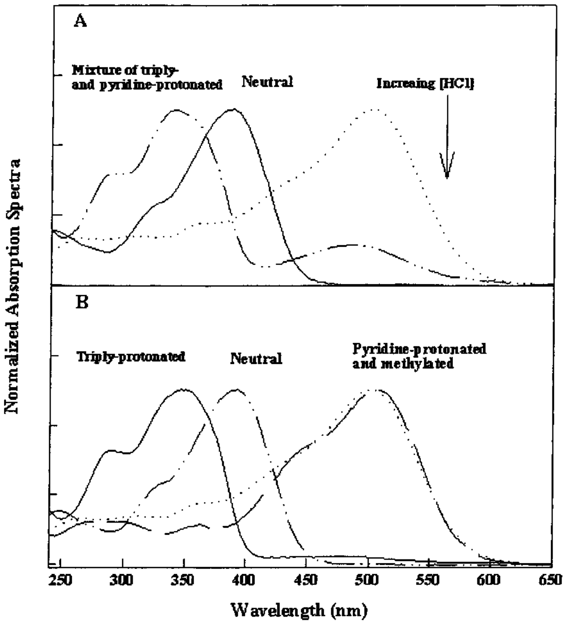


Figure 5. Protonation effects on absorption spectrum of compound **V**. In **A**, neutral (—); addition of dilute HCl (pyridine-protonated) (···) and pyridine-protonated compound with gradual addition of dilute HCl; mixture of aniline and pyridine protonation (—··—). In **B**, neutral (—··—); triply protonated (—); pyridine-protonated (···) and methylated compound **VI** in methanol (- -).

ethylaniline moieties. To test this hypothesis we triply protonated compound **III** and determined that its absorption and fluorescence are blue shifted to 364 nm and λ_{max} 423 nm, respectively; essentially superimposable with the published spectrum of 2,6-distyryl pyridine (λ_{max} 365 nm, fluorescence λ_{max} 425 nm).[14,15] By extrapolation this result implies that the absorption spectra of the exhaustively protonated compounds **VI** and **V** also correspond to loss of the dimethylanilino lone pairs to conjugation and cyanine formation.

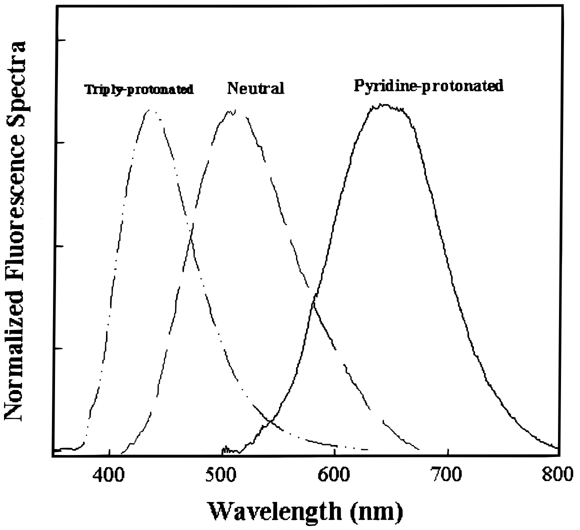


Figure 6. Protonation effects on emission spectrum of compound **V**. Fluorescence spectra of the neutral (- -), pyridine-protonated (—) and triple-protonated compound **V** (—··—).

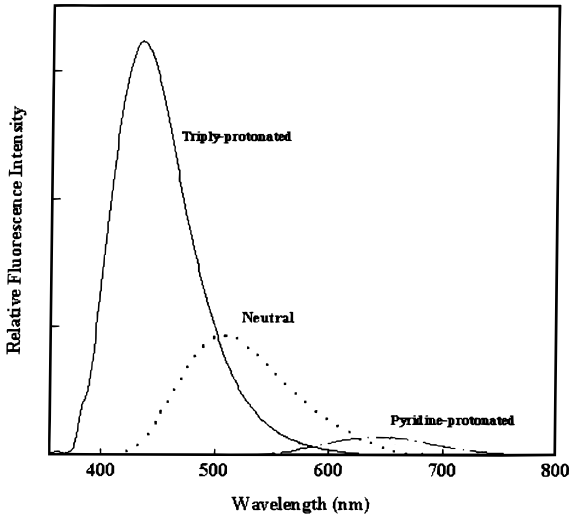


Figure 7. Acid effect on fluorescence intensity of compound **V** in methanol: neutral, (···); after addition of concentrated HCl (aniline-protonated), (—). Compound **V** after addition of dilute HCl (pyridine-protonated) (- -). Excitation for each solution was at their absorption peak maxima, keeping the same optical density.

Protonation of the eight pyridylvinylene compounds also produces significant effects on their emission properties such as wavelength and quantum yield. Figure 6 shows the fluorescence spectra of neutral, pyridine-protonated and triply protonated forms of compound **V**. The pyridine-protonated and triply protonated spectra exhibit red and blue shifts, respectively, compared with their neutral form. In general, the pyridine-protonated or methylated compound in polar solvents, such as methanol, has a smaller quantum yield than the neutral compound as shown in Table 1. For instance, in methanol, the quantum yields of neutral (**V**) and pyridine-protonated **V** are 0.005 and 0.002, respectively, and 0.01 and 0.003 for neutral (**I**) methylated (**II**) model compounds, respectively. However, triple-protonation results in an even higher quantum yield than observed for the neutral system ($\Phi_F = 0.009$) as shown in Figure 7. The low fluorescence quantum yields in the neutral compounds could be due to the formation of charge-transfer interactions between the donor aniline moiety and the acceptor pyridine moiety in their excited states or through a photoinduced twisted intramolecular charge transfer (TICT) process.[24-28] Rettig[28,29] and Fromhertz[24,25] have reported that compounds **II**, **VIII** and similar pyridylvinylene derivatives show TICT states with different single bond or double bond rotations. In general, the charge transfer process is non emissive or weakly fluorescent and competes with fluorescence.[29] Upon triple-protonation, this process is shut down and therefore, fluorescence increases. The very low quantum yield observed with only pyridine nitrogen quaternization is fully in line with the hypothesis set forth above that protonation removes dross conjugation; i.e., the action of protonation renders the oligomer "*p*-doped". It is well-known that *p*-doping of PPV shuts down its fluores-

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cence.[30] Qualitatively, the solid state fluorescence of either the triply protonated species [**III**-$(H^+)_3$, **V**-$(H^+)_3$] or the doubly protonated [**IV**-$(H^+)_2$, **VI**-$(H^+)_2$] salts is much stronger than the emission of the same species in solution, making these compounds potential solid-state acid sensors. For example, very brief exposure of a silica gel-adsorbed sample of any of the four species mentioned above to HCl vapor, changes its color and luminescence (under 366 nm irradiation) from very weak blue to very strong greenish-white.

Control experiments indicate that protonated pyridylvinylene derivatives can be easily deprotonated by adding base and the optical properties of the resulting deprotonated compounds are identical to those of the neutral compounds, demanding the not unexpected conclusion that protonation is fully reversible.

Conclusion

A series of cross-conjugated, donor−acceptor-donor types of bis-substituted pyridylvinylene derivatives were synthesized and their primary optical properties were reported. It was found that the optical properties of these compounds are very sensitive to solvent polarity and pH. Based on absorption and emission properties of the neutral and methylated compounds, pyridine and multiple protonation of the neutral compounds can be easily distinguished spectroscopically. It was concluded that the first protonation of the neutral compounds occurs on the nitrogen atom of the pyridine ring, which significantly red shifts the absorption by ∼100 nm, close to 70 nm more than in the 2,5-isomeric polymer.[31] Following the first protonation, triple-protonation, in which additional protonation occurs on the nitrogen atom of the dimethylaniline moieties takes place. This produces a blue-shift of absorption and fluorescence as well as a dramatic increase in fluorescence quantum yield, especially in the solid state. These changes occur concurrent with a shutdown of the charge-transfer process in the excited state.

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