

New Star-Shaped Molecules with Extended Electronic Delocalization

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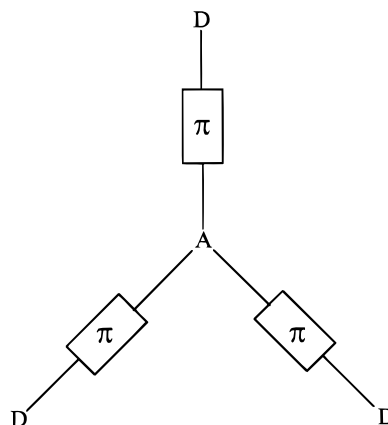
New star-shaped molecules have been easily prepared with cyanuric chloride and some pyridine derivatives. These molecules present an important electronic delocalization between the attractive central ring and the three end donor groups. Molecular modeling by ab initio and PM3 semiempirical methods shows that the molecules belong to the D_{3h} group. These trications display one reduction wave for which the formal redox potentials have been determined.

Introduction

There is increasing interest in the synthesis of new symmetrical molecules with trigonal or hexagonal symmetry, based on a symmetrically substituted benzenoid aromatic ring, with long-range electron delocalization.¹ This interest arises as well from the peculiar behavior of these molecules due to their unusual steric and electronic configuration, than from their potentially attractive properties in fields such as three-dimensional conducting polymers² or nonlinear optics.³ Especially, the planar push–pull molecules with a D_{3h} symmetry are believed to display a second-order nonlinearity of octupolar origin.^{3b–e}

We were particularly interested in the preparation and study of molecules of D_{3h} symmetry in which the central ring plays an electron-attracting role while the substituted chains possess a conjugated electron-releasing group as pictured below (Scheme 1). Aromatic nucleophilic substitution is a convenient means to introduce nucleophilic substituents on aromatic ben-

Scheme 1. Electronic Structure of Octupolar Molecule in C_3 Symmetry



with A : Attractive group

D : Donor group

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zenoid rings; in particular, several interesting new cationic compounds were recently prepared starting from hexafluorobenzene^{4,5} or trifluorobenzene.⁵ We have applied this type of reaction to the synthesis of a new family of three-branched trications with the general formula shown in Scheme 2.

Along with the final star-shaped trications, we report improved syntheses of some 4-styrylpyridines which are

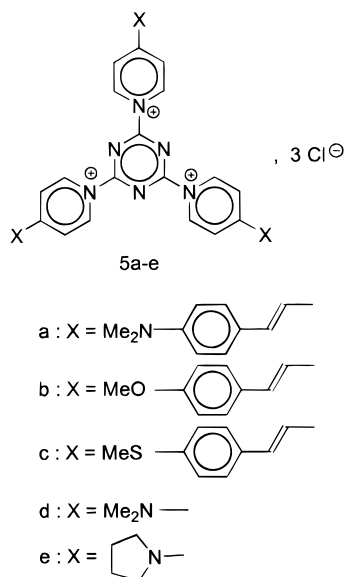
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Scheme 2. General Formula of New Star-shaped Molecules (5)



the precursors of the final compounds. Electrochemistry of the trications is also presented, as well as the results of computer calculations giving the most probable conformation of the molecules and the influence of the substituents on the molecule conformation.

The HOMO and LUMO energies of the molecules have been calculated and allow to explain the dependence of the electrochemical data on the electron-donating character of the substituents.

Results and Discussion

Synthesis of the Molecules. The difficulty in the synthesis of 4-styrylpyridines with donor groups is that

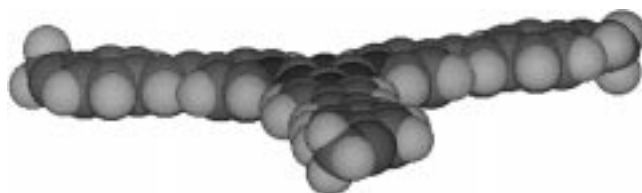


Figure 1. 3D optimized structure of **5b** calculated using the PM3 semiempirical method.

the classical aldol condensation is difficult to perform, due to the low electrophilicity of the donor group substituted aldehydes. Some authors have therefore proposed other ways, including boron trifluoride catalyzed condensation⁶ or vinyl-aryl palladium catalyzed coupling.⁷ Although reported yields are good to average, these methods suffer from the use of expensive catalysts which require cautious handling. In fact, the classical aldol condensation was found to occur easily with good yields using the potassium *tert*-butoxide/DMF couple as base and solvent, respectively, which has proved to be the most successful, especially with donor substituents.

Analogous replacement of halogens has been recently described with activated pyridines, and especially (dimethylamino)pyridine (DMAP), on an activated pyrimidine ring⁸ or cyanuric chloride.⁹ The nucleophilic character of the 4-styrylpyridines is comparable to that of standard pyridines bearing identical substituents; therefore the substitution took place smoothly within 2 h upon gentle warming with cyanuryl chloride in ethyl acetate, to give the trisubstituted adduct as sole product.

Besides the chloride counteranions arising directly from the synthesis, the trications have been prepared in association with iodide or hexafluorophosphate anions, by exchange with the appropriate sodium or tetraammonium salt. However, the solubility in common solvents was found to decrease, so the chloride still

Table 1. UV-Visible Spectroscopic Studies of Star-Shaped Molecules (5)

star-shaped molecules (5)	λ_{\max} (nm)	extinction coeff ($\times 10^3 \text{ L} \cdot \text{mol}^{-1} \text{ m}^{-1}$)	energies correlated to λ_{\max} (eV)
2,4,6-tri[1-[4-[4-(dimethylamino)styryl]pyridinium]]-1,3,5-triazine trichloride (5a)	547 (intense purple)	2.88	2.27
2,4,6-tri[1-[4-[4-(methoxy)styryl]pyridinium]]-1,3,5-triazine trichloride (5b)	440 (deep orange)	2.75	2.82
2,4,6-tri[1-[4-[4-(thiomethyl)styryl]pyridinium]]-1,3,5-triazine trichloride (5c)	470 (red)	2.73	2.64
2,4,6-tri[1-[4-(dimethylamino)pyridinium]]-1,3,5-triazine trichloride (5d)	432 (orange yellow)	1.22	2.87
2,4,6-tri[1-(4-pyrrolidinopyridinium)]-1,3,5-triazine trichloride (5e)	310 (pale yellow)	1.05	3.03

Table 2. Molecular Modeling and Electrochemistry Studies of Star-Shaped Molecules

star-shaped molecules (5)	HOMO and LUMO energies (eV)			reduction potentials (V/SCE)	
	RHF/3-21G*	PM3	RHF/3-21G*/PM3	E_{p1}^a	E_{p2}^a
2,4,6-tri[1-[4-[4-(dimethylamino)styryl]pyridinium]]-1,3,5-triazine trichloride (5a)	-16.91	-16.42	-16.77	-0.71	-1.08
2,4,6-tri[1-[4-[4-(methoxy)styryl]pyridinium]]-1,3,5-triazine trichloride (5b)	-6.84	-9.62	-7.08	-0.545	-1.08
		-14.02	-13.38		
2,4,6-tri[1-[4-[4-(thiomethyl)styryl]pyridinium]]-1,3,5-triazine trichloride (5c)		-8.83	-6.56	-0.485	-0.98
		13.35	-8.87		
2,4,6-tri[1-[4-(dimethylamino)pyridinium]]-1,3,5-triazine trichloride (5d)	-12.40	13.02	12.35	-1.10 ^b	-1.41
	-5.64	-7.87	-5.70		
2,4,6-tri[1-(4-pyrrolidino)pyridinium]-1,3,5-triazine trichloride (5e)	-16.57	-16.21	-16.43	-1.10 ^b	-1.42
	-6.51	-9.39	-6.78		
2,4,6-tri[1-pyridinium]-1,3,5-triazine trichloride		-14.78	14.17		
		-9.45	-7.11		

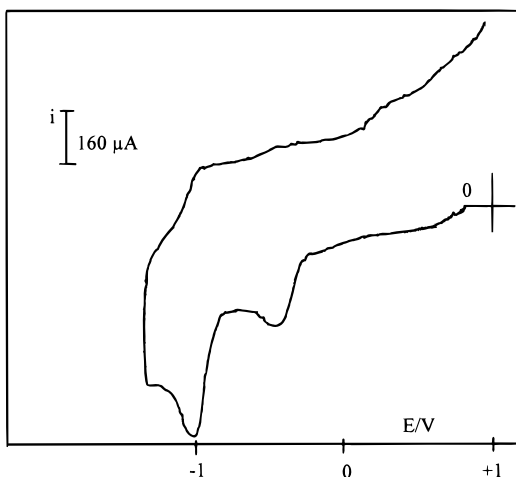


Figure 2. Cyclic voltammogram of a solution of **5c** ($C^\circ = 10^{-3}$ mol l^{-1} in acetonitrile solution ($+0.1$ mol l^{-1}) NEt_4ClO_4) on a 3 mm diameter glassy carbon electrode. (Scan rate = 1.0 V s^{-1}).

seems to be the most suitable counteranion for further investigations on the trications. However it should be noticed that hydrolysis of the trication counteranions plays an important role toward the reactivity of these compounds toward nucleophilic attack. Unfortunately, anions such as hexafluorophosphate, which give the

trications the best resistance against nucleophilic displacement, also led to the poorest solubilities in common solvents.

Attempts to reduce the trications were unsuccessful, using potassium borohydride or surprisingly even lithium aluminum hydride. Probably this is a consequence of the fact that the charge on the nitrogen atoms is extremely delocalized and therefore the styrylpyridines are highly insensitive to nucleophilic attack.

UV-Visible Studies. The molecules of type **5** display only one absorption band in the UV-visible range in DMSO. The extinction coefficients have been determined (Table 1); the compounds are produced as powders, and their colors are also given in Table 1.

Molecular Modeling of the Star-Shaped Molecules. The optimized geometries of the new trications (**5a,d,e**) have been calculated using ab initio calculations at the RHF/3-21G* level without imposing any symmetry onto the system. In all cases, molecules were found to be planar with a D_{3h} symmetry. Due to the length of the calculations, we checked that similar configurations were obtained with the semiempirical PM3 method. HOMO and LUMO energies were calculated with both methods for molecules **5a,d,e** at the RHF/3-21G*/RHF/3-21G* and the RHF/3-21G*/PM3 levels. Calculations were performed with the Gaussian

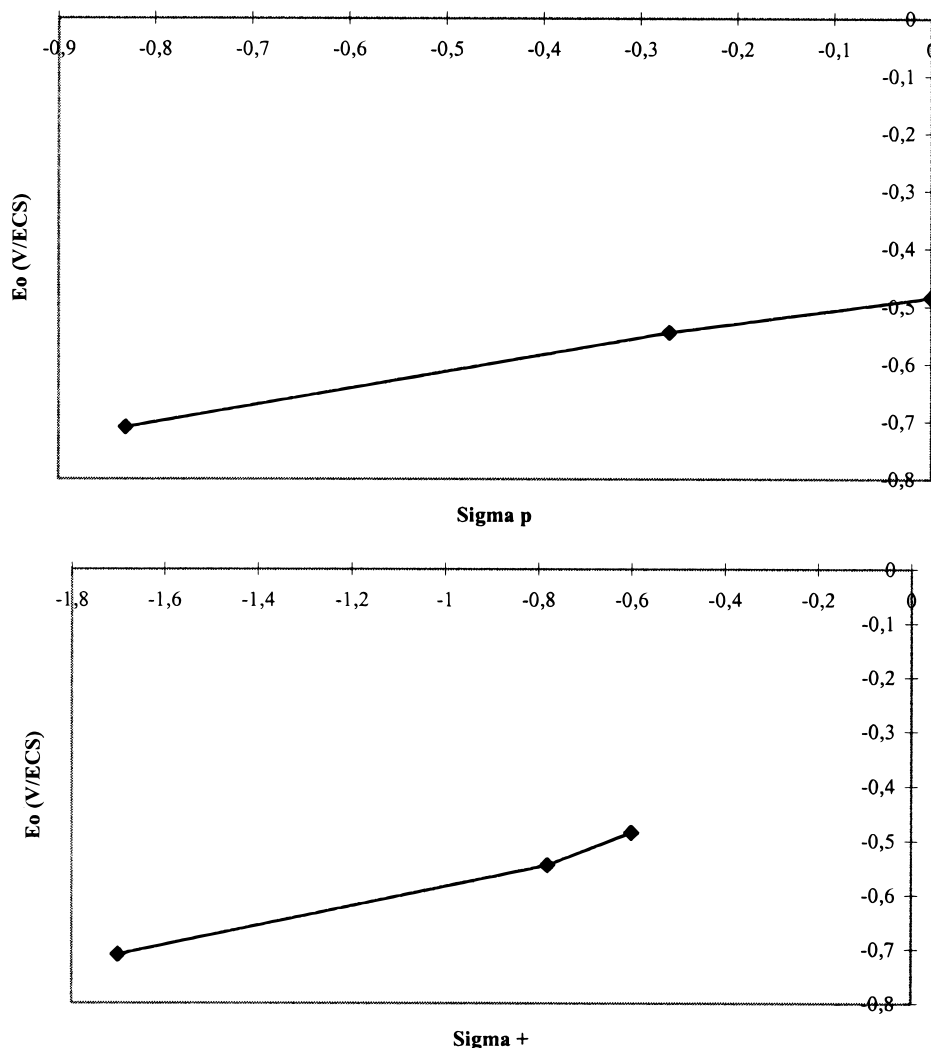


Figure 3. Variation of reduction standard potentials, E° , with Hammett coefficients σ^+ or σ^p .

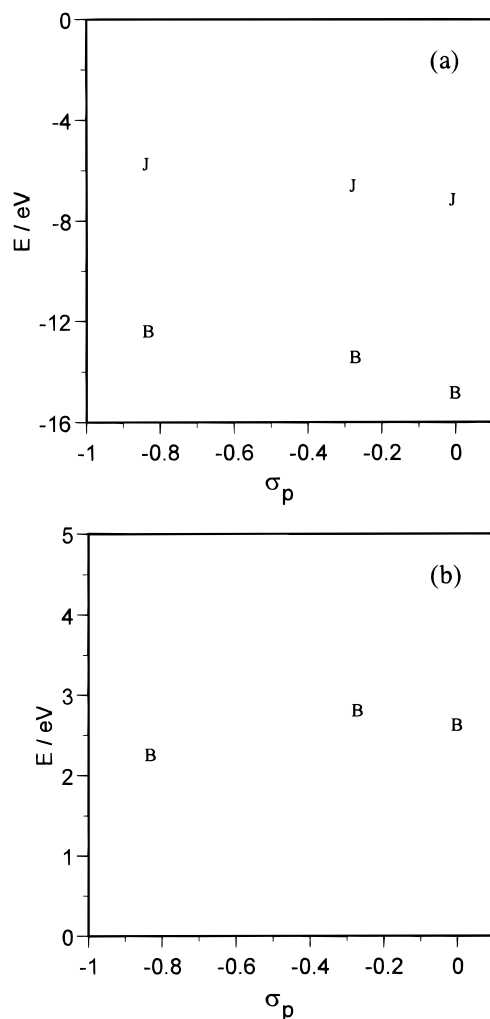


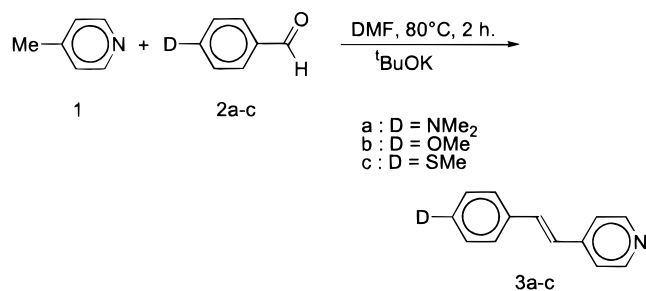
Figure 4. Variations of (a) the HOMO (J) and LUMO (B) orbital energies and (b) the energies correlated to λ_{max} with the Hammett coefficients σ_p .

G94W package.⁹ From the molecular modeling, the molecules' space group is D_{3h} ; therefore, optical nonlinearity of octupolar origin should be encountered as in, for example, crystal violet.^{3c}

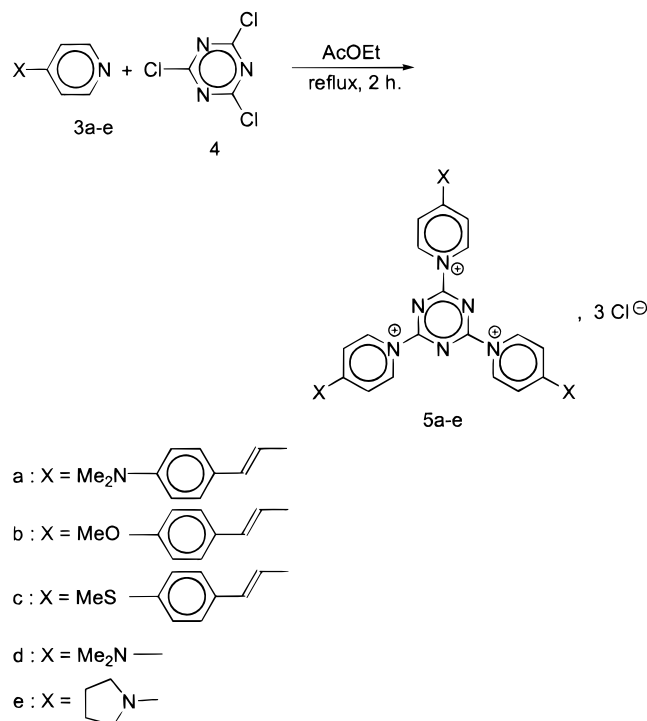
The energy values (Table 2) obtained by the RHF/3-21G*/RHF/3-21G* and RHF/3-21G*/PM3 calculations are in very good agreement for molecules **5a**, **-d**, and **-e**, so we can suppose that this is also the case for the other trications. The dependence of the HOMO and LUMO energies on the Hammett coefficients is represented in Figure 4a. It is clear that a better correlation is obtained with the LUMO than with the HOMO energies.

Electrochemistry. The reductive electrochemical behavior of all trications has been examined in DMSO. All compounds exhibit two one-electron reduction waves, as displayed in Figure 2. In the case of the styrylpyridine-derived trications, the first electron transfer may

Scheme 3. Synthesis of 4-Donor Styrylpyridine (**3**)



Scheme 4. Synthesis of 2,4,6-Tri[1-pyridinium]-1,3,5-triazine Trichloride (**5**)



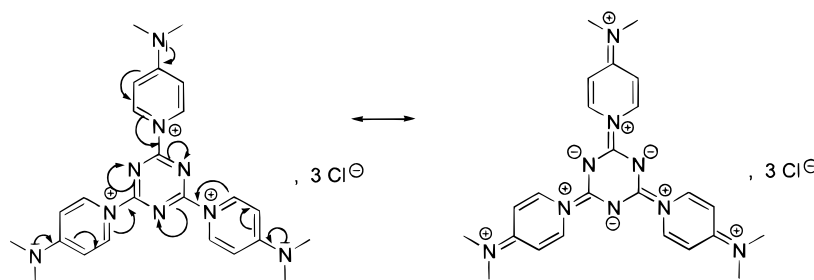
be rendered reversible upon increasing the scan rate above 50 V/s. With the two other cations, the kinetics of the electron transfer are not fast enough to reach such scan rates and only the peak potentials have been determined. All electrochemical data are listed in Table 2. Although there is much evidence of extended electronic delocalization in the trications (Scheme 5), the electrogenerated dication radicals are not stable upon slow cycling.

The redox potentials of the trications correlate with either the σ_p or σ^+ values of the end substituent (according to Taft)¹⁰ with almost the same slope (Figure 3), thus confirming the electronic conjugation along the substituted branches and the good correlation of the LUMO energies with the substituent effects, as predicted by molecular calculations (Figure 4a). The energies associated with the maximum absorption wavelengths (Table 1) are correlated with the electronic gap values of the molecules. However, these values do not correlate with the electronic effects of the substituents, as shown in Figure 4b. This can also be related to the

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Scheme 5. Limits Formula for Star-Shaped Molecule 5d



results of molecular calculations displayed in Table 2, which show that the HOMO energies are more sensitive to the substituent than the LUMO and do not follow accurately the Hammett correlation.

Conclusion

We have reported the synthesis and some characteristics of new star-shaped molecules. Molecular modeling as well as electrochemical studies show that there is extended electronic delocalization on the three branches. The nonlinear optical properties of these molecules are under investigation.

Experimental Section

^1H and ^{13}C NMR spectra were recorded on a Bruker Spectrospin AC 200 spectrometer in $\text{DMSO-}d_6$. UV-visible spectra were recorded on a Beckman DU 650 spectrophotometer in DMSO. Analytical data were performed by the CNRS Vernaison (France). 4-Picoline, 4-(dimethylamino)pyridine, 4-pyrrolidinopyridine, 4-dimethylaminobenzaldehyde, 4-methoxybenzaldehyde, 4-methylthiobenzaldehyde, and cyanuric chloride were Aldrich products and were used without further purification.

Synthesis of 4-Styrylpyridine (3a–c): General procedure (Scheme 3). A mixture of 10 mmol of 4-picoline, 12 mmol of potassium *tert*-butoxide, and 10 mmol of aromatic aldehyde (respectively, 4-dimethylaminobenzaldehyde (**2a**), 4-methoxybenzaldehyde (**2b**), or 4-methylthiobenzaldehyde (**2c**)) was introduced into 50 mL of anhydrous DMF and heated for 2 h at 80 °C under efficient magnetic stirring. After cooling at room temperature, the mixture was added to 200 mL of dichloromethane and washed once with 200 mL of ice-water and then three times with 200 mL of aqueous 1 M potassium hydroxide. The organic phase was separated, dried on sodium sulfate, and evaporated. The crude solid was recrystallized in the appropriate solvent.

Spectroscopic Data for Compounds 3

4-[4-(Dimethylamino)styryl]pyridine (3a). Yield: 92% (recrystallized in toluene). Mp: 245–46 °C; Lit. 245–47 °C. ^1H NMR: δ 3.00 (s, 6H, NMe_2), 6.77 (d, $J = 8.92$ Hz, 2H), 6.98 (d, $J = 16.37$ Hz, 1H), 7.45 (d, $J = 16.20$ Hz, 1H), 7.51 (d, $J = 6.08$ Hz, 2H), 7.54 (d, $J = 8.91$ Hz, 2H), 8.51 ppm (d, $J = 6.09$ Hz, 2H). ^{13}C NMR: δ 40.28, 112.20, 117.93, 122.07, 122.89, 130.18, 140.60, 141.62, 151.76, 154.92 ppm.

4-[4-(Methoxy)styryl]pyridine (3b). Yield: 94.8% (recrystallized in cyclohexane). Mp: 95 °C; Lit. 95 °C. ^1H NMR: δ 3.82 (3H, s, OMe), 7.02 (d, $J = 8.72$ Hz, 2H), 7.12 (d, $J = 16.50$ Hz, 1H), 7.52 (d, $J = 16.40$ Hz, 1H), 7.53 (d, $J = 6.07$ Hz, 2H), 7.64 (d, $J = 8.72$ Hz, 2H), 8.55 ppm (d, $J = 5.92$ Hz, 2H). ^{13}C NMR: δ 55.58, 114.39, 120.69, 123.58, 128.65, 128.84, 132.75, 144.71, 150.04, 159.82 ppm.

4-[4-(Methylthio)styryl]pyridine (3c). Yield: 90% (recrystallized in cyclohexane). Mp: 118–20 °C. ^1H NMR: δ 2.55 (s, 3H, SMe), 7.24 (d, $J = 17.40$ Hz, 1H), 7.33 (d, $J = 8.40$ Hz, 2H), 7.55 (d, $J = 17.60$ Hz, 1H), 7.58 (d, $J = 6.17$ Hz, 2H),

7.64 (d, $J = 8.35$ Hz, 2H), 8.57 ppm (d, $J = 6.09$ Hz, 2H). ^{13}C NMR: δ 14.49, 120.86, 125.11, 125.93, 127.65, 132.55, 132.77, 139.20, 144.44, 150.10 ppm.

Synthesis of 2,4,6-tri-[1-Pyridinium]-1,3,5-triazine trichloride (5) general procedure (Scheme 4). Upon mechanical stirring, a solution of 5.0 mmol of nucleophile (respectively, 4-[4-(dimethylamino)styryl]pyridine (**3a**), 4-[4-(methoxy)styryl]pyridine (**3b**), 4-[4-(methylthio)styryl]pyridine (**3c**), 4-(dimethylamino)pyridine (**3d**), or 4-pyrrolidinopyridine (**3e**)) in 50 mL of anhydrous ethyl acetate was added to 1.67 mmol of cyanuric chloride in 10 mL of the same solvent and refluxed for 2 h. The solid precipitate was recovered, washed three times with 50 mL of anhydrous acetone, and dried in a vacuum to give the trications (**5a–e**).

Spectroscopic Data for Compounds 5

2,4,6-Tri[1-[4-[4-(dimethylamino)styryl]pyridinium]]-1,3,5-triazine Trichloride (5a). Yield: 1.35 g (94.7%). Mp: >300 °C. ^1H NMR: δ 3.05 (s, 18H, NMe_2), 6.83 (d, $J = 7.53$ Hz, 6H), 7.25 (d, $J = 15.91$ Hz, 3H), 7.65 (d, $J = 7.63$ Hz, 6H), 7.90 (d, $J = 15.84$ Hz, 3H), 8.00 (d, $J = 4.05$ Hz, 6H), 8.75 ppm (d, $J = 4.1$ Hz, 6H). ^{13}C NMR: δ 40.69, 117.02, 121.20, 122.68, 131.73, 138.15, 138.35, 150.07, 152.81, 158.38, 162.44 ppm. Anal. Calcd for $\text{C}_{48}\text{H}_{48}\text{Cl}_3\text{N}_9 \cdot 5\text{H}_2\text{O}$: C, 60.85; H, 6.17; N, 13.31%. Found: C, 60.97; H, 6.27; N, 13.26%. $\lambda_{\text{max}} = 547$ nm.

2,4,6-Tri[1-[4-[4-(methoxy)styryl]pyridinium]]-1,3,5-triazine Trichloride (5b). Yield: 1.32 g (97.4%). Mp: >300 °C. ^1H NMR: δ 4.05 (s, 9H, OMe), 7.25 (d, $J = 8.72$ Hz, 6H), 7.35 (d, $J = 16.40$ Hz, 3H), 7.85 (d, $J = 16.10$ Hz, 3H), 7.88 (d, $J = 6.07$ Hz, 6H), 7.98 (d, $J = 8.72$ Hz, 6H), 8.85 ppm (d, $J = 5.92$ Hz, 6H). ^{13}C NMR: δ 55.63, 114.84, 121.08, 122.51, 130.78, 131.07, 157.44, 158.53, 156.62, 161.83, 162.80 ppm. Anal. Calcd for $\text{C}_{45}\text{H}_{39}\text{N}_6\text{Cl}_3\text{O}_3 \cdot 5\text{H}_2\text{O}$: C, 59.50; H, 5.44; N, 9.25%. Found: C, 59.66; H, 5.64; N, 9.21%. $\lambda_{\text{max}} = 440$ nm.

2,4,6-Tri[1-[4-[4-(thiomethyl)styryl]pyridinium]]-1,3,5-triazine trichloride (5c). Yield: 1.40 g (97.5%). Mp: >300 °C. ^1H NMR: δ 2.56 (s, 9H, SMe), 7.35 (d, $J = 8.32$ Hz, 6H), 7.46 (d, $J = 16.80$ Hz, 3H), 7.75 (d, $J = 8.14$ Hz, 6H), 7.93 (d, $J = 16.37$ Hz, 3H), 8.07 (d, $J = 6.60$ Hz, 6H), 8.85 ppm (d, $J = 6.08$ Hz, 6H). ^{13}C NMR: δ 14.19, 123.26, 129.32, 138.33, 143.15, 143.42, 149.15, 157.12, 158.26, 159.57, 162.65 ppm. Anal. Calcd for $\text{C}_{45}\text{H}_{39}\text{N}_6\text{Cl}_3\text{S}_3 \cdot 5\text{H}_2\text{O}$: C, 56.51; H, 5.16; N, 8.79%. Found: C, 56.65; H, 5.28; N, 8.74%. $\lambda_{\text{max}} = 470$ nm.

2,4,6-Tri[1-[4-(dimethylamino)pyridinium]]-1,3,5-triazine Trichloride (5d). Yield: 0.97 g (95%). Mp: >300 °C. ^1H NMR: δ 3.22 (s, 18H, NMe_2), 7.05 (d, $J = 7.53$ Hz, 6H), 8.25 ppm (d, $J = 7.63$ Hz, 6H). ^{13}C NMR: δ 40.69, 107.49, 136.75, 157.03, 162.27 ppm. Anal. Calcd for $\text{C}_{24}\text{H}_{30}\text{Cl}_3\text{N}_9 \cdot 5\text{H}_2\text{O}$: C, 44.97; H, 6.29; N, 19.66. Found: C, 45.10; H, 6.64; N, 19.58%. $\lambda_{\text{max}} = 432$ nm.

2,4,6-Tri[1-(4-pyrrolidino)pyridinium]-1,3,5-triazine Trichloride (5e). Yield: 1.00 g (95.6%). Mp >300 °C. ^1H NMR: δ 2.07 ppm (t, $J = 6.66$ Hz, 12H), 3.73 (t, $J = 6.70$ Hz, 12H), 7.05 (d, $J = 7.99$ Hz, 6H), 9.36 ppm (d, $J = 7.86$ Hz, 6H). ^{13}C NMR: δ 27.71, 49.35, 108.15, 136.67, 155.06, 162.12 ppm. Anal. Calcd for $\text{C}_{24}\text{H}_{36}\text{Cl}_3\text{N}_9 \cdot 5\text{H}_2\text{O}$: C, 44.55; H, 7.16; N, 19.48. Found: C, 44.76; H, 7.36; N, 19.44%. $\lambda_{\text{max}} = 310$ nm.

Electrochemistry

Cell and Electrodes. The counter electrode was a Pt wire, and the reference electrode was an aqueous saturated calomel electrode ($E^\circ/\text{SCE} = E^\circ/\text{NHE} - 0.2412 \text{ V}$) with a salt bridge containing the supporting electrode. The working electrode was a 3 mm diameter glassy carbon disk. The SCE electrode was checked against the ferrocene/ferricinium couple ($E^\circ = +0.405 \text{ V/SCE}$) after each set of experiments. All the potentials are reported versus SCE.

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Instrumentation and Procedures. Electrochemical instrumentation consisted of a PAR model 175 universal programmer and a home-built potentiostat equipped with a positive feedback compensation device.¹¹ The cathodic and anodic peaks were measured on a Nicolet 310 digital oscilloscope. The overall accuracy of the normal potential determinations was usually $\pm 5 \text{ mV}$, except in the case of the 2,4,6-tri[1-[4-(dimethylamino)styryl]pyridinium]-1,3,5-triazine trichloride (**5a**), because the low solubility of this compound obliged us to work below $5 \times 10^{-4} \text{ M}$, and the accuracy is about 10 mV in this case.

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