

New Chelating Stilbazonium-Like Dyes from Michler's Ketone

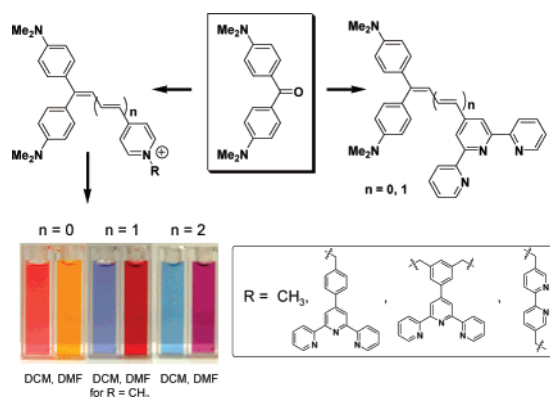
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ABSTRACT



A series of "push-pull" salts substituted with an electron-donating bis(*N,N*-dimethyl)aniline unit and different electron-withdrawing methyl or chelating pyridinium units have been designed and synthesized from Michler's ketone. The spectroscopic and electronic properties were investigated and compared to their DAST homologues. The studies revealed that a lower HOMO–LUMO gap is obtained in all cases, showing the ability of our donor to increase the "push-pull" effect. Two chromophores with a terpyridine as acceptor end group have also been prepared.

Electro-optic (EO) and nonlinear optical (NLO) properties of organic dyes have attracted considerable attention because of their potential applications in optical data processing technologies.¹ These chromophores are based on a push-pull system, which consists of an electron-donating group (D) and an electron-withdrawing group (A) coupled through a π -conjugated spacer. The molecular properties of the chromophores depend on the strength of the "push-pull" effects which are functions of the ability of the donor to

provide electrons and the acceptor to withdraw electrons. The efficiency of the dye can be enhanced by introducing a better donor and/or a better acceptor. Concerning pure organic chromophores exhibiting intense NLO response, "push-pull" molecules bearing *N,N*-dimethylaniline as donating group have been widely studied.² In the solid state, organic crystals of 4-(4-*N,N*-dimethylaminostyryl)-1-methylpyridinium tosylate (DAST) are of particular interest because they have the largest NLO coefficient among organic materials.³ In that case, the acceptor is the methyl pyridinium

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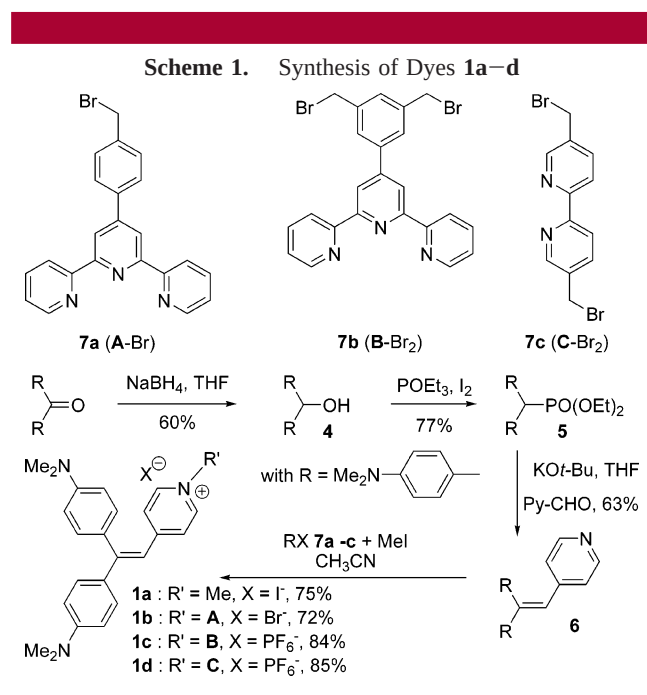
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group. But recent research has also shown that metal complexes offer many possibilities. Several systems where the acceptor is a pyridine chelated to a metal have also been reported.⁴ Our research group is involved in the design and investigation of metal complexes for the conception of nanocomposites exhibiting electrochemical properties and photoluminescence at room temperature.⁵ In the course of our studies, it was interesting to investigate new chromophores bearing on one side two *N,N*-dimethylaniline groups as donating moiety and on the other side ligands able to coordinate metals as accepting moiety. Herein, we report the preparation and properties of these chromophores linked to ligands such as terpyridine and bipyridine via a methylpyridinium group. Two chromophores with a terpyridine as the acceptor end group have been prepared.

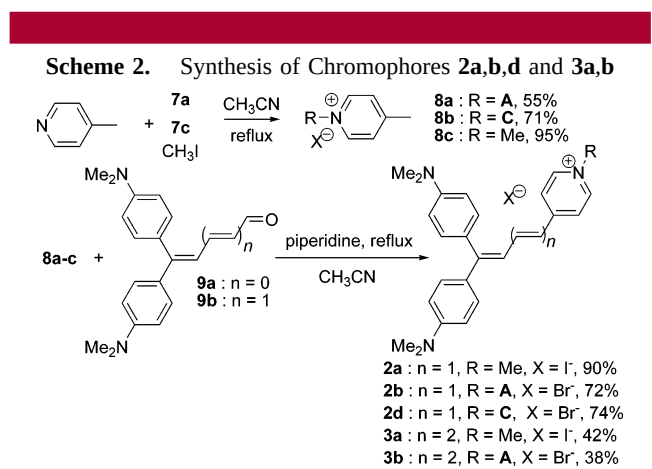
Chromophores **1a–d**, **2a–d**, and **3a,b** have been prepared according to two different strategies. The first one, used for the synthesis of **1a–d**, consisted of the preparation of molecule **6**, which is an interesting building block as it can be further functionalized to obtain various donor–acceptor systems that are amenable to further functionalization. Molecule **6** was obtained in three steps starting from the commercially available Michler's ketone (Scheme 1).



Alcohol **4** was obtained in moderate yield by reduction of the Michler's ketone with sodium borohydride in boiling THF and was then directly converted to the phosphonate **5**

using a procedure described in the literature.⁶ Molecule **6** was finally synthesized using a Horner–Wadsworth–Emmons olefination. The generation of a carbanion from **5** proceeded smoothly by treatment with the non-nucleophilic base KO^tBu , and the desired molecule was obtained in moderate yield (63%). Reaction of 1 equiv of methyl iodide, brominated terpyridine **7a,b**, or bipyridine **7c** with molecule **6** at reflux for one night in acetonitrile afforded the salts **1a–d** with yields ranging from 72% to 85%. Terpyridine **7b**, used in the previous reaction, has been obtained differently from the literature,⁷ in 67% yield, by bromination of 4'-(3,5-bis-methylphenyl)[2,2',6',2'']terpyridine) with NBS and benzoyl peroxide in CCl_4 .

Pyridine derivatives **2a,b,d** and **3a,b** bearing extended conjugated olefinic substituent in an all-trans configuration were obtained by a second procedure as illustrated in Scheme 2.



In the first step, three different *N*-substituted pyridinium **8a–c** were prepared from 4-picoline and the corresponding halogenated derivative **7a,c** or methyl iodide, respectively. Then base-catalyzed condensations of aldehydes **9a,b** with salts **8a–c** in the presence of piperidine afforded the chromophores **2a,b,d** and **3a,b** with yields ranging from 38% to 90%. The Knoevenagel reaction furnished each dye as a mixture of cis/trans isomers, with the trans isomer as the major product in all cases. Isomerization with diluted iodine in a mixture of toluene and chloroform afforded all-trans configuration dyes, except **3b**, which was never fully isomerized. To facilitate the purification of the salts and to increase the solubility, bromide salts **1c** and **1d** were converted to the corresponding hexafluorophosphate ones.

Due to the side products formed during the synthesis of **2b** and **2d** and the difficulties in separating them from the target molecule, a third method was developed to obtain an extended analogue of pyridine **6**. Moreover, this molecule can be easily used to functionalize various bromo derivatives.

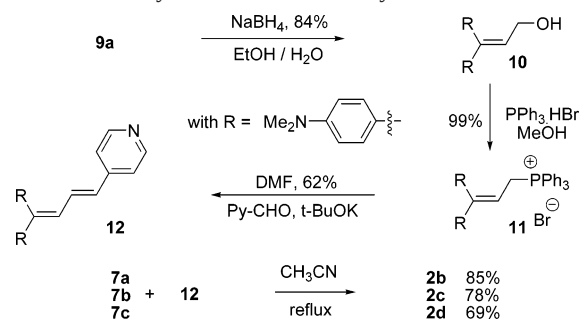
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Molecule **12** was obtained in three steps as outlined in Scheme 3. Aldehyde **9a** was reduced with sodium borohydride in ethanol to give the alcohol **10** in 84%

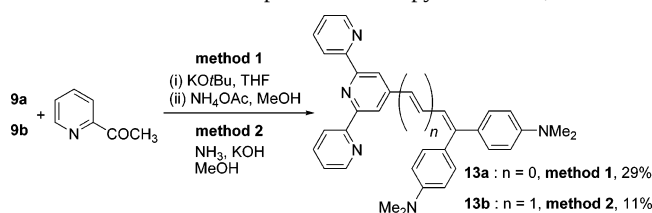
Scheme 3. Synthesis of All-*trans* Pyridine **12** and **2b–d**



yield. It was then converted to the phosphonium **11** using 1 equiv of phosphonium hydrobromide in methanol at room temperature for 4 days. Finally, pyridine **12** was prepared by a Wittig reaction with the phosphonium **11** and pyridine-4-carboxaldehyde. All-*trans* isomerization was achieved by treatment with iodine in toluene at reflux. Pyridine **12** was obtained in 62% yield. Finally, salts **2b–d** were prepared according to the same procedure used for **1a–d**. All obtained dyes are orange or black in the solid state and freely dissolve in polar solvents to produce orange or violet solutions.

We also investigated the synthesis of chromophores with a terpyridine as accepting end group (Scheme 4). The

Scheme 4. Preparation of Terpyridines **13a,b**



terpyridine **13a** was synthesized using the Kröhnke methodology.⁸ The terpyridine core was prepared by condensation of the aldehyde **9a** with 2-acetylpyridine in the presence of KO^tBu and NH₄OAc. Surprisingly, when the reaction was carried out in the same conditions with the aldehyde **9b**, the expected terpyridine **13b** was not obtained but the decomposition of the aldehyde **9b** was observed instead. **13b** was finally obtained by a one-pot procedure using a mixture of 2-acetylpyridine and the aldehyde **9b** in alkaline methanolic solution, as previously reported in the literature.⁹

The absorption spectra recorded for the acetonitrile solution of the dyes **1a**, **2a**, and **3a** are shown in Figure 1. These

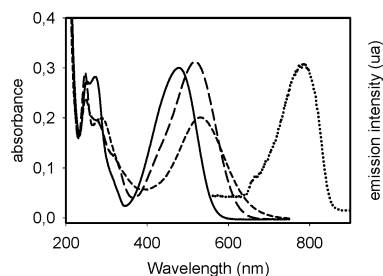


Figure 1. UV–vis spectra of dyes **1a** (solid line), **2a** (short dashed line), and **3a** (dashed line) at 20 °C in acetonitrile (0.5 mM) and emission (dotted line) spectrum of **2a** in acetonitrile. The sample was excited at 471 nm for the luminescence spectrum.

dyes have the same methylpyridinium iodide accepting moiety but differ from the number of ethylenic conjugated spacers ($n = 0–2$). All of the dyes exhibit three transitions and cover a broad range (250–750 nm) of the UV–vis spectrum. Each dye shows an intense visible absorption due to intramolecular charge transfer (ICT) excitations and less intense bands ascribed to nondirectional $\pi \rightarrow \pi^*$ transitions at higher energy.

As expected, these ICT bands red shift as n increases. The same phenomenon is observed with dyes **1b**, **2b**, and **3b**. Compared to DMF, the absorption maxima obtained for **1a**, **2a** and **3a** in dichloromethane are strongly shifted. The greatest shift is observed for the dye **3a** with $\Delta\lambda = 83$ nm. Examination of the solvatochromism for each dye in seven solvents revealed a good correlation with the solvent parameters π^* determined by Kamlet and Taft (Table 1).¹⁰

Table 1. Absorption Maxima (nm) Obtained Experimentally by UV–vis Spectroscopy and π^* Values by Kamlet and Taft for Dyes **1a**, **2a**, and **3a**

solvent	π^*	λ_{max} (1a)	λ_{max} (2a)	λ_{max} (3a)
toluene	0.54	475	527	545
THF	0.58	484	524	550
MeOH	0.60	484	521	535
acetone	0.71	480	521	533
CH ₃ CN	0.75	478	519	530
CH ₂ Cl ₂	0.82	523	589	613
DMF	0.88	478	518	530
DMSO	1	468	520	535

The negative solvatochromism observed for **1a**, **2a**, and **3a** was expected¹² and reflects a decrease of the ground state dipole moment of the dye molecules upon excitation. The

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HOMO–LUMO gap can be experimentally calculated from the position of the ICT band. A stronger decrease of the gap occurs from $n = 0$ to $n = 1$ ($\Delta E = 0.2$ eV) compared with the gap difference observed from $n = 1$ to $n = 2$ ($\Delta E = 0.05$ eV). The variation of the gap value from $n = 0$ to $n = 1$ can be explained by the steric hindrance between the aromatic groups in **1a**, steric hindrance that indeed decreases with the lengthening of the ethylenic spacer.

The HOMO–LUMO gap was also investigated by cyclic voltammetry. The cathodic part corresponds to the reversible reduction of the pyridinium moiety, which is shifted toward more positive potentials as n increases.

The anodic part exhibits a much more complicated behavior with three non reversible signals followed by a reversible adsorption–desorption process (Figure 2).

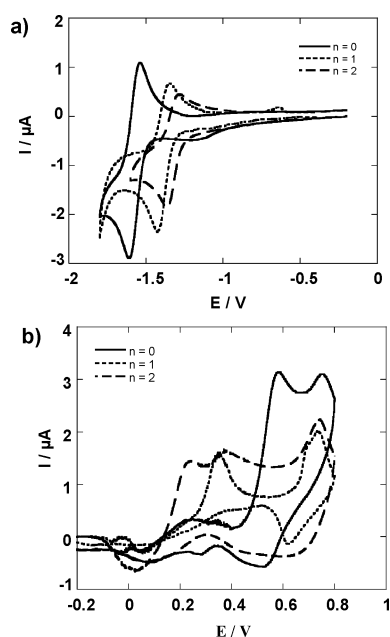


Figure 2. Cyclic voltammograms (CVs) of dyes **1a** (solid line, $n = 0$), **2a** (short dashed line, $n = 1$), and **3a** (dashed line, $n = 2$) at 20 °C in dichloromethane + TBAPF₆ (ca. 2 mM) on platinum electrodes at 50 mV/s: (a) cathodic part, (b) anodic part. For clarity, the signal due to oxidation of the iodide counterion was subtracted by recording CV of TBAI.

In such conditions the first redox peak can be ascribed to the irreversible oxidation of the vinyl moiety into cation radical followed by dimerization:¹⁴ the corresponding oxidation potential is strongly shifted to less positive values as n increases, since the radical created is more stabilized by a longer polyvinyl spacer. This redox step is followed by the irreversible oxidation of the dimethylaniline end functions

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at ca. +0.75 V (almost independently on n) in the previously oxidized products, involving precipitation of the coupling products on the electrode.

The lack of chemical reversibility for these oxidation processes prevents us from measuring true standard potentials, leading only to minimal values for the band gap measured from the difference between oxidation potential of the donor and reduction potential of the acceptor (Table 2). Nevertheless, the results obtained by this second technique

Table 2. HOMO–LUMO Gap Obtained Experimentally by UV–vis Spectroscopy and Cyclic Voltammetry in Acetonitrile for Dyes **1a**, **2a**, and **3a**

dyes	ΔE^a (eV)	ΔE^b (eV)	DAST	
			analogues, $n =$	ΔE^c (eV)
1a	> 2.18	2.59	0	2.64
2a	> 1.75	2.39	1	2.55
3a	> 1.56	2.34	2	2.48

^a Results from cyclic voltammetry in CH₂Cl₂. ^b Results from UV–vis spectroscopy in CH₃CN. ^c Data taken from ref 11.

clearly exhibit the same trend for the variation of E_g according to the value of n as those given by UV–vis spectroscopy. Comparison of the HOMO–LUMO gap determined for our dyes with reported dyes (DAST and extended analogues) bearing only one *N,N*-dimethylaniline group^{11,13} as donor shows that in all cases, the gap obtained for Michler’s derivatives is smaller. Comparison of both donors revealed that Michler’s donating group is the strongest of the two groups (Table 2). Photoluminescence studies showed that, compared to DAST, all three dyes **1a**, **2a** and **3a** have rather weak fluorescence in acetonitrile, as shown in Figure 1 for chromophore **2a** (see the Supporting Information). The largest Stokes shift of fluorescence emission is obtained for **2a** (~250 nm). The emission intensity drops to about 10% of the intensity observed for DAST. A stronger decrease in luminescence intensity occurs upon replacement of the methyl pyridinium by other groups (terpyridyl for **2b** and bipyridyl for **2d**).

In conclusion, we have succeeded in the development of a family of new dyes bearing two *N,N*-dimethylaniline groups as donor and ligands such as terpyridine and bipyridine as acceptor. Such ligands can be used to prepare metal complexes, currently studied in our laboratory. Thus, these chromophores are potential candidates for advanced materials applicable to optoelectronic fields, such as nonlinear optics.

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Supporting Information Available: Experimental procedures and spectroscopic characterizations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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