

# New Second-Order NLO Chromophores Based on 3,3'-Bipyridine: Tuning of Liquid Crystal and NLO Properties

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We report on the synthesis via a Knoevenagel condensation reaction of a new family of push–pull molecules based on 6,6'-distyryl-3,3'-bipyridine. These chromophores were characterized by spectroscopic methods (NMR, UV–vis, photoluminescence), their mesogenic behavior was investigated by DSC and optical microscopy, and their second-order NLO properties were evaluated by the electric field second harmonic (EFISH) technique. All the compounds are transparent at the second harmonic wavelength of typical laser sources (1.32 and 1.55  $\mu\text{m}$ ), and some of them exhibit a strong emission. By lateral substitutions of the  $\pi$ -conjugated bridge and by varying the nature of the acceptor/donor pair, we were able to tune both the mesogenic and NLO properties of the chromophores. For the mesogenic chromophores, first hyperpolarizabilities extrapolated to infinite wavelength,  $\beta_0$ , between  $16 \times 10^{-30}$  and  $85 \times 10^{-30}$  esu were measured. These compounds exhibit enhanced hyperpolarizabilities compared to typical NLO liquid crystal chromophores reported in the literature.

## 1. Introduction

Organic systems with second-order nonlinear optical (NLO) properties have been intensively studied due to their potential applications such as second harmonic generation (SHG), optical parametric oscillation (OPO) and electrooptic modulation (EO).<sup>1–5</sup> Among these materials are polymers and more particularly side-chain polymers (SCPs). In SCPs, active chromophores are covalently bound on the polymer backbone as side chains. The chromophore consists of an asymmetric  $\pi$ -conjugated charge transfer (CT) organic molecule containing both electron-acceptor and -donor groups connected by an electron-transmitting bridge. The second-order NLO properties of the material originate from the

noncentrosymmetric alignment of the chromophores under the application of an electric field (poling). However, upon removal of the poling field, the NLO chromophore orientation is lost due to the mobility of both side chains and polymer backbone. An attractive alternative to side-chain isotropic polymers are therefore side-chain liquid crystal polymers (SCLCPs) in which the NLO chromophores possess mesogenic properties.<sup>6</sup> Indeed, it has been shown, both theoretically<sup>7,8</sup> and experimentally<sup>9–11</sup> that SCLCPs can attain, enhance and retain the high degree of noncentrosymmetric order required for second-order susceptibility  $\chi^{(2)}$  applications. For example, values of second harmonic coefficient  $d_{33}$  up to 30–35 pm.V<sup>-1</sup> were obtained with 4-cyano-4'-hydroxybiphenyl-based nematic polymers.<sup>9–11</sup> These weakly resonant and stable values compete with those of inorganic materials such as potassium titanyl phosphate (KTP) or lithium niobate (LiNbO<sub>4</sub>) on one hand, with those of isotropic SCPs<sup>12</sup> on the other hand. Despite these promising results, a large number of studies have

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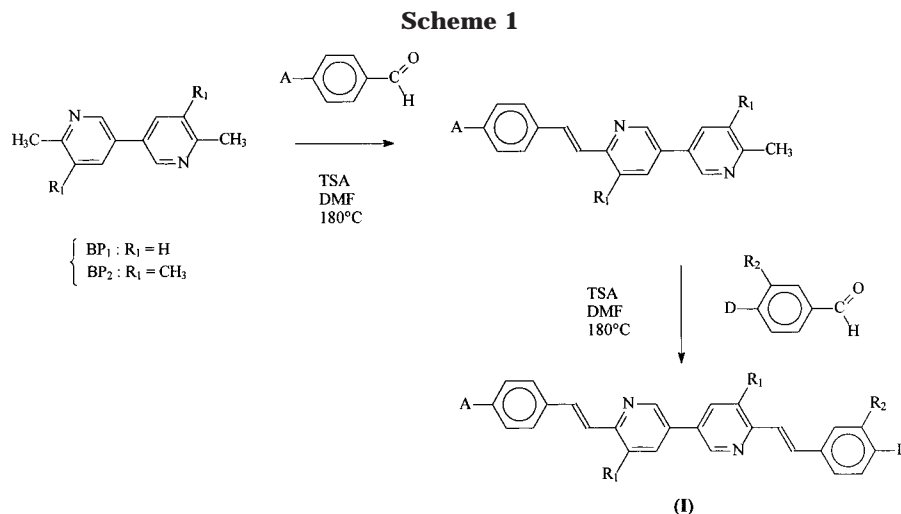
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core	R <sub>1</sub>	R <sub>2</sub>
1	H	H
2	CH <sub>3</sub>	H
3	CH <sub>3</sub>	CH <sub>3</sub>
4	CH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>

A/D pair	A	D
a	CN	OC <sub>6</sub> H <sub>13</sub>
b	NO <sub>2</sub>	OC <sub>6</sub> H <sub>13</sub>
c	CN	N(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>
c*	CN	NC <sub>6</sub> H <sub>13</sub>
d	NO <sub>2</sub>	N(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>
d*	NO <sub>2</sub>	NC <sub>6</sub> H <sub>13</sub>

been dedicated to molecular engineering<sup>13–15</sup> of traditional push–pull molecules leading to compounds displaying giant static quadratic hyperpolarizabilities  $\beta_0^{16}$  (i.e., up to  $1500 \times 10^{-30}$  esu). Meanwhile, there are fewer studies on NLO mesogenic chromophores<sup>17–19</sup> and their molecular NLO remain modest ( $\beta_0$  ranging from  $5 \times 10^{-30}$  to  $35 \times 10^{-30}$  esu). In this context, it is worth to design and synthesize new mesogenic efficient NLO chromophores.

In previous papers,<sup>20,21</sup> we reported a strategy to synthesize new liquid crystalline 6,6'-distyryl-3,3'-bipyridine derivatives. They were obtained via a Knoevenagel condensation reaction of 6,6'-dimethyl-3,3'-

bipyridine or 5,5',6,6'-tetramethyl-3,3'-bipyridine, with aromatic aldehydes para-substituted with electron donor (*n*-hexyloxy) or acceptor (cyano) groups. This led to symmetric compounds bearing one hexyloxy or cyano group at each end of the electron transmitting bridge. The study of their mesophases gave a first insight in the tuning of the mesogenic behavior with chemical structure. It appeared that *n*-hexyloxy end substitutions favor the occurrence of smectic mesophases, whereas cyano end substitutions only led to nematic phases. Moreover, it has been demonstrated that lateral disubstitution of the bipyridine core by methyl groups decreases liquid crystal thermal stability.

In the present work, we have been interested in designing asymmetric chromophores (see Structure I in Scheme 1) with (i) donor/acceptor (D/A) pairs of various strength and (ii) various R<sub>1</sub> and R<sub>2</sub> groups as lateral substituents, to tune mesogenic and NLO properties. All the synthesized soluble chromophores (Chart 1) were characterized by means of <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies, differential scanning calorimetry (DSC), optical microscopy, UV/visible and fluorescence spectroscopies, and electric field induced second harmonic generation technique (EFISH) in solution. Specific properties which are of interest are the liquid crystalline behavior and the molecular NLO response. In all cases, these properties were analyzed and discussed in terms of nature of the conjugated core and end-substituent effects.

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Chart 1

Compound	Chemical structure
a1	
a2	
a4	
b2	
b3	
b4	
c1	
c*2	
d1	
d*2	

## 2. Experimental Section

**2.1. Reagents.** The syntheses and analytical characteristics of 6,6'-dimethyl-3,3'-bipyridine (BP<sub>1</sub>) and 5,5',6,6'-tetramethyl-3,3'-bipyridine (BP<sub>2</sub>) have been previously reported.<sup>19</sup> Benzoic anhydride, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *p*-toluenesulfonic acid monohydrate (TSA), piperazine, *n*-bromohexane, 4-fluorobenzaldehyde, 4-cyanobenzaldehyde, 4-nitrobenzaldehyde, 4-hexyloxybenzaldehyde, 3-methyl-4-hydroxybenzaldehyde, and 3-ethoxy-4-hydroxybenzaldehyde (all from Aldrich) were used without further purification.

**2.2. Syntheses.** *4-(Piperazino)benzaldehyde.* A total of 21 g (0.242 mol) of piperazine, 15 g (0.121 mol) of 4-fluorobenzaldehyde, 32 g (0.242 mol) of K<sub>2</sub>CO<sub>3</sub>, and 90 mL of DMSO were introduced into a two-necked round-bottom flask fitted with a condenser and an argon inlet. The mixture was then stirred for 36 h at 90 °C. The mixture was cooled to room temperature and poured into water. The crude product recov-

ered by filtration was washed with water and ethyl acetate. Finally, 5.166 g of pure 4-(hydroxypiperazino)benzaldehyde was obtained as a white powder (yield: 23%).

*4-(Hexylpiperazino)benzaldehyde, 3-Methyl-4-hexyloxybenzaldehyde, and 3-Ethoxy-4-hexyloxybenzaldehyde.* They were prepared by alkylation of 4-(piperazino)benzaldehyde, 3-methyl-4-hydroxybenzaldehyde, and 3-ethoxy-4-hydroxybenzaldehyde, respectively, with bromohexane, under basic conditions (K<sub>2</sub>CO<sub>3</sub>) in DMSO, according to the literature procedure.

*4-(Hexylpiperazino)benzaldehyde.* <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ [ppm]: 0.88 (m, 3H), 1.29 (m, 6H), 1.50 (m, 2H), 2.36 (m, 2H), 2.56 (t, 4H, <sup>3</sup>J(H,H) = 5.1 Hz), 3.39 (t, 4H, <sup>3</sup>J(H,H) = 5.1 Hz), 6.90 (d, 2H, <sup>3</sup>J(H,H) = 8.8 Hz), 7.73 (d, 2H, <sup>3</sup>J(H,H) = 8.8 Hz), 9.76 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ [ppm]: 14.0, 22.6, 26.8, 27.2, 31.7, 47.1, 52.8, 58.7, 113.4, 127.0, 131.8, 155.0, 190.3.

The general procedure for the syntheses and characterizations of monosubstituted derivatives (6-(4-cyanostyryl)-6'-

Table 1. Phases Transitions of Studied Compounds

Compound	Phase - T <sup>a</sup> (°C) - [ΔH <sup>b</sup> (J.g <sup>-1</sup> )]
<b>a1</b>	K - 120.7 [19.5] - S <sub>B</sub> - 185/205 - S <sub>A</sub> - 233.7 [6.9] - N - 302.5 [0.34] - I
<b>a2</b>	K - 179.9 [124.6] - N - 287.7 [3.2] - I
<b>a4</b>	K - 165.5 [92.7] - I
<b>b2</b>	K - 92.4 [91] - N - 281.3 [1.9] - I
<b>b3</b>	K - 178 [67.6] - I
<b>b4</b>	K - 150.4 [66.7] - I
<b>c1</b>	K - 256.4 [48.6] - I
<b>c*2</b>	K - 202.9 [52.2] - N - 327.3 [0.9] - I
<b>d1</b>	K - 244.8 [36.6] - I
<b>d*2</b>	K - 193.3 [67.3] - N - > T <sub>d</sub> (>285) - I

<sup>a</sup> T: transition temperature. <sup>b</sup> ΔH: enthalpy change determined by DSC. Notation: K, crystal; S<sub>X</sub>, smectic of type X; N, nematic; I, isotropic liquid; T<sub>d</sub>, decomposition temperature.

methyl-3,3'-bipyridine, 6-(4-cyanostyryl)-5,5',6'-trimethyl-3,3'-bipyridine, 6-(4-nitrostyryl)-6'-methyl-3,3'-bipyridine, and 6-(4-nitrostyryl)-5,5',6'-trimethyl-3,3'-bipyridine) is given as Supporting Information.

The syntheses and analytical characteristics of 6-(4-cyanostyryl)-6'-(4-hexyloxy)styryl)-3,3'-bipyridine (**a1**) and 6-(4-cyanostyryl)-6'-(4-hexyloxy)styryl)-5,5'-dimethyl-3,3'-bipyridine (**a2**) have been previously reported.<sup>18,19</sup> Compounds **a4**, **b2**, **b3**, **b4**, **c1**, **c\*2**, **d1**, and **d\*2** were prepared by the same procedure from the appropriate monosubstituted derivative and aldehyde. Their syntheses, <sup>1</sup>H and <sup>13</sup>C NMR data, and elemental analyses are given as Supporting Information.

**2.3. Techniques.** Nuclear Magnetic Resonance (NMR) Spectroscopy. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Unity 300 spectrometer operating at 299.95 and 75.144 MHz, respectively. Chloroform-*d* (CDCl<sub>3</sub>) was used as solvent and tetramethylsilane (TMS) as internal standard.

**Thermal Analysis.** The transition temperatures were measured using a differential thermal analyzer (Dupont 1090) operating at 20 °C/min under nitrogen.

**Phase Behavior.** Optical textures were observed under a polarizing microscope (Nachet) equipped with a Mettler Toledo FP82HT hot stage and a Mettler Toledo FP90 central processor.

**Optical Spectroscopies.** The UV-visible absorbance spectra were recorded on a spectrometer Perkin-Elmer Lambda 18. A 1 cm quartz cell was used and the concentrations were chosen so that the appropriate absorbance values (0.1–0.2) were obtained at λ<sub>max</sub>. The extinction coefficients were determined from the absorption measurement of at least five different solutions in dichloromethane with concentrations typically ranging from 5 × 10<sup>-5</sup> to 10<sup>-6</sup> M. The fluorescence spectra were obtained using a Aminco-Bowman Series 2 luminescence spectrometer. Fluorescence quantum yields were measured in ethyl acetate solutions by comparison with emission of P60 in acetonitrile for which a value of 0.73 has been taken.

**Determination of the Onsager Radius *a*.** The radii *a* of the equivalent spheres, meaning the volume inside a contour of 0.001 electron/bohr<sup>3</sup> density, were obtained by means of a volume calculation on the AM1-optimized geometry. The used radius was 0.5 Å larger than the radius corresponding to the computed volume as recommended to estimate the Onsager radius.<sup>22</sup> Calculation and optimization were carried out with the Gaussian G98 package.<sup>23</sup>

**Determination of the Oscillator Strength *f*.** The absorption band shape is fairly symmetrical and can be treated as a Lorentzian function. If the extinction coefficient at the maximum (ε<sub>max</sub>) and the half-width at half-maximum (ΔV<sub>1/2</sub>) are measured,<sup>18</sup> then *f* = 4.32 × 10<sup>-9</sup> ε<sub>max</sub>ΔV<sub>1/2</sub>.<sup>24</sup>

**Electric Field Induced Second Harmonic Generation (EFISH) Technique.** Second-order molecular hyperpolarizability coefficients of the chromophores were measured in solution (chro-

mophores concentrations of 5 × 10<sup>-3</sup> to 10<sup>-2</sup> mol L<sup>-1</sup> in dichloromethane) at 1.32 μm by the electric field induced second harmonic (EFISH) technique.<sup>25,26</sup> The laser source is continuum Nd<sup>3+</sup>-YAG laser operating at 1.32 μm and emitting 40 ns pulses with 10 Hz repetition rate.

### 3. Results and Discussion

**3.1. Synthesis.** The synthetic route of the push-pull molecules, shown in Scheme 1, is a two-step Knoevenagel condensation, under acidic conditions, of 6,6'-dimethyl-3,3'-bipyridine (BP<sub>1</sub>) or 5,5',6,6'-tetramethyl-3,3'-bipyridine (BP<sub>2</sub>) with aromatic aldehydes para-substituted with electron acceptor (A) or donor (D) group. (A) is a cyano or a nitro group, (D) is an alkoxy (*n*-hexyloxy) or an amino group (dibutylamino or hexylpiperazino). All the chromophores synthesized (Chart 1) were characterized and identified by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies and found to be pure by elemental analyses. Moreover, they present two trans vinylene units, evidenced by the three bond coupling constant (<sup>3</sup>J<sub>H,H</sub> ≈ 16 Hz) in <sup>1</sup>H NMR spectra.

**3.2. Mesomorphic Behavior.** The thermal behavior of all the compounds has been studied by differential scanning calorimetry (DSC) and polarizing microscopy. The transition temperatures, the nature of the phases, and the enthalpy changes are reported in Table 1.

At first, the cyano and *n*-hexyloxy groups were employed because they are classical acceptor and donor groups used in NLO. Moreover they are known to favor the formation of nematic and smectic phases, respectively.<sup>27</sup> This was observed in a previous work<sup>18</sup> with **a1**, which forms mesophases which were all identified: the molecule presents different smectic phases (S<sub>B</sub> and S<sub>A</sub>) and its smectic-nematic transition temperature

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appears at 233.7 °C. This high temperature for the apparition of the nematic phase and the formation of the low fluid phase  $S_B$  are not favorable for a poling process in polymer, later on.

To destabilize the LC character and to lower the transition temperature, a methyl group ( $R_1$ ) was introduced as lateral substituent on the pyridinic ring. This assumption is clearly demonstrated in the case of **a2**, which is purely nematogenic. Moreover, the K/N transition temperature is decreased (179.9 °C for **a2** instead of 233.7 °C for **a1**), the N/I transition temperature as well (287.7 vs 302.5 °C for **a2** and **a1**, respectively). Moreover, the substitution of a phenyl ring in meta position with the  $R_2$  group (methyl or ethoxy) gives **a4**, which does not exhibit any mesogenic behavior, as evidenced in Table 1.

Because the nitro group is a more efficient acceptor group,<sup>1-3</sup> compound **b2** was then synthesized. Note that the nitro group is reported in the literature as a less efficient group for the formation of nematic phases than the cyano one. However, texture observations by polarizing microscopy indicate that **b2** forms only enantiotropically nematic *Schlieren* textures in the LC range (from 192.4 to 281.3 °C). As for the **a** series, **b3** and **b4** were prepared with a methyl and an ethoxy group, respectively, as  $R_2$ . In both cases, the liquid crystal character is suppressed. The isotropization temperature of **b4** is lower than those of **b3** (150.4 and 178 °C for **b4** and **b3**, respectively): the bigger the steric hindrance of the lateral group, the more important the destabilizing effect on the isotropization temperature.

To use a stronger donor group than the *n*-hexyloxy one, an amino group<sup>1-3</sup> was employed: in particular, the dibutylamino group. In this case, contrary to previous chromophores, derivatives based on core **1** (**c1** and **d1**) do not exhibit any mesogenic behavior, whatever the acceptor group (cyano or nitro). In addition, their melting temperatures are rather high (K/I transition temperature ( $T_{KI}$ ) equal to 256.4 and 244.8 °C for **c1** and **d1**, respectively). To obtain liquid crystal homologues of **c1** and **d1**, one method consists of constraining the amine in a cycle.<sup>28</sup> This was achieved by using the hexylpiperazino group as terminal group. So, **c\*2** and **d\*2** were synthesized. As evidenced by DSC and optical microscopy, they exhibit only a broad nematic phase (from 202.9 to 327.3 °C for **c\*2** and from 193.3 to more than 285 °C for **d\*2**).

For all the mesogenic compounds, the large liquid crystal range ( $\sim 100$  °C) and the high isotropization temperature found ( $T_{NI}$  above 280 °C) show their good thermal stability.

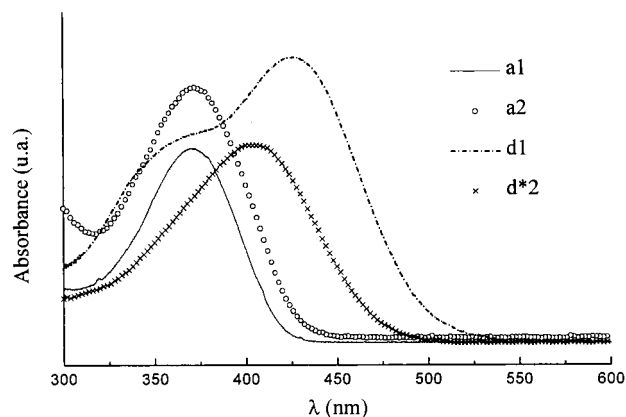
**3.3. Linear Optical Properties.** All linear optical measurements (i.e., absorption and emission spectra) have been performed in solution on a wide range of solvent polarity (from  $\epsilon = 2.21$  for dioxane to  $\epsilon = 46.45$  for DMSO).

*Absorption.* for all compounds, only the absorption maxima ( $\lambda_{max}$ ) in dichloromethane are reported in Table 2, because no noticeable solvatochromic shift is observed

**Table 2. Linear (Absorption Maximum  $\lambda_{max}$  and Cut-Off  $\lambda_{cut-off}$ ) and Nonlinear Optical Data ( $\mu\beta$  Measured at 1.32  $\mu\text{m}$ ,  $\mu\beta_0$  and  $\beta_0$ ) in Dichloromethane<sup>a</sup>**

compd	LC	absorption $\lambda_{max}$ (nm) [ $\lambda_{cut-off}$ (nm)]	NLO properties		
			$\mu\beta$ , 10 <sup>-48</sup> esu ( $\pm 10\%$ )	$\mu\beta_0$ , 10 <sup>-48</sup> esu ( $\pm 10\%$ )	$\beta_0$ , <sup>b</sup> 10 <sup>-30</sup> esu ( $\pm 10\%$ )
<b>a1</b>	X	373 [435]	150	95	19
<b>a2</b>	X	374 [444]	130	80	16
<b>a4</b>		376 [441]	<sup>c</sup>	<sup>c</sup>	<sup>c</sup>
<b>b2</b>	X	391 [465]	325	195	30-40
<b>b3</b>		389 [465]	305	185	30-40
<b>b4</b>		392 [467]	305	185	30-40
<b>c1</b>		418 [508]	1200	645	90-130
<b>c*2</b>	X	398 [482]	510	295	40-60
<b>d1</b>		426 [530]	1480	775	110-155
<b>d*2</b>	X	406 [500]	765	430	60-85
<i>DR1</i>		486	1240	510	60

<sup>a</sup> Notations: LC, liquid crystal;  $\mu$ , dipole moment in the ground state;  $\beta$ , first hyperpolarizability;  $\beta_0$ , first hyperpolarizability extrapolated to infinite wavelengths. <sup>b</sup> Calculated with  $\mu_{a1} = \mu_{a2} = 5$  D,  $\mu_{DR1} = 9$  D, and  $5$  D  $< \mu < 7$  D for others. <sup>c</sup> NLO properties not evaluated; the values should be close to the ones of **a1** and **a2** because (i) **a1**, **a2**, and **a4** have the same linear optical properties (absorption and emission) and (ii) **b2**, **b3**, and **b4** have the same linear and nonlinear optical properties.



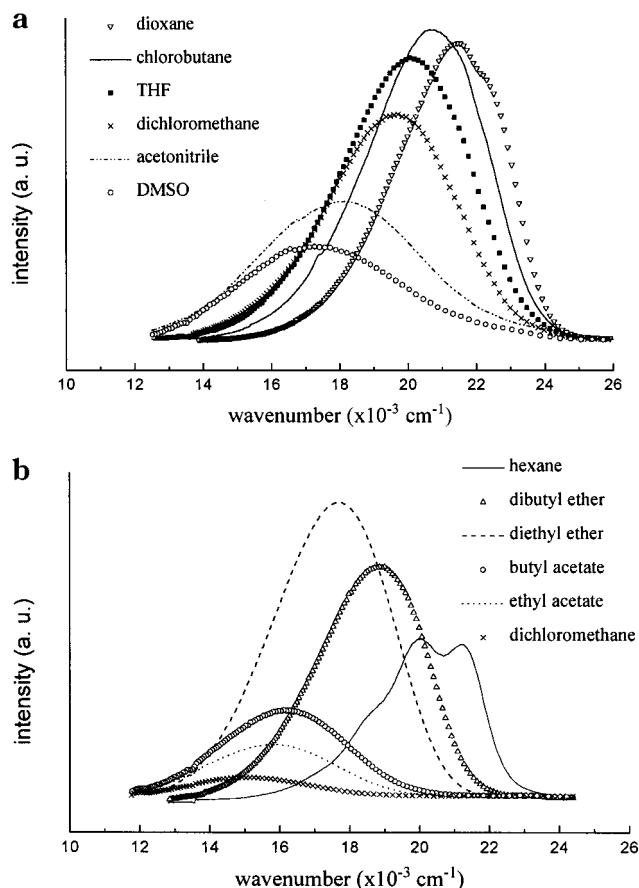
**Figure 1.** Absorption spectra of **a1**, **a2**, **d1**, and **d\*2** in dichloromethane.

for all the chromophores, in contrast to typical NLO ones such as *p*-nitroaniline (PNA) or 4-*N,N*-dimethylamino-4'-nitrostilbene (DANS).<sup>1-3</sup> The values of  $\lambda_{max}$  lie in the range of 372 nm for **a1** to 426 nm for **d1**. Representative absorption spectra are displayed in Figure 1 for chromophores **a1**, **a2**, **d1**, and **d\*2**. The main features of the spectra are an intense, low lying (near the UV region) absorption band for compounds bearing a *n*-hexyloxy group. Concerning the spectra of amino chromophores, they usually present a shoulder (**d1**), which is not observable for **d\*2**. The large molar absorption coefficients (values of  $\epsilon > 50000$  L mol<sup>-1</sup> cm<sup>-1</sup>) are indicative of highly  $\pi$ -conjugated systems.

The influence of D/A pair on the optical properties is also clearly evidenced. On one hand, when increasing the D/A strength, a red shift (see Figure 1 for **a1** and **d\*2**) is observed. This is consistent with an improve charge transfer and that enlightens that the  $\pi$ -bridge in these 3,3'-bipyridine derivatives is efficient. On the other hand, the structure of the end substituent could also have a significant effect on the linear optical properties, as shown for the amino group: for series **c** and **d**, the cyclization of the amine induces an hypsochromic shift of the absorption band ( $\sim 20$  nm for **c\*2**

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**Figure 2.** Solvent effect on the emission spectra of compounds **a2** (a) and **c1** (b).

and **d\*2** compared to **c1** and **d1**, respectively). We can assume that there is a steric hindrance between the piperazino ring and the adjacent phenyl ring which impedes a good delocalization of the charges. So, the charge transfer is less efficient in the case of the hexylpiperazino group compared to the dibutylamino one.

In contrast, there is no significant difference between chromophores within series **a** (see **a1** and **a2** in Figure 1; **a1**, **a2**, and **a4** in Table 2) and **b** (Table 2). This fact proves that  $R_1$  and  $R_2$  do not influence the optical properties of the chromophores.

From the applicative point of view, Figure 1 enlightens a very interesting feature of the chromophores: they exhibit a low cutoff wavelength (lower than 530 nm). So, these molecules present an optical transparency at the second harmonic wavelengths of typical laser sources (1.3 and 1.55  $\mu\text{m}$ ).

**Photoluminescence.** At first note that only chromophores bearing the cyano group as electron acceptor moiety exhibit fluorescence. Typical evolutions of the emission spectra according to the solvent polarity are presented in Figure 2, parts a and b, for compounds **a2** and **c1**, respectively.

The mean feature of the emission spectra of **a2** and **c1** is a broad emission band, except for **c1** in hexane. In the latter case, a structured emission is observed with two distinct peaks at 21200 and 19900  $\text{cm}^{-1}$  and a shoulder at about 18700  $\text{cm}^{-1}$ . The mean distance between component peaks is on average 1100  $\text{cm}^{-1}$ . This value is consistent with vibronic couplings in the ground

state, attributed to phenyl or heterocyclic C–H bending energy.

Concerning the solvatochromic effect in emission, in the case of the cyano/*n*-hexyloxy substituted chromophore (**a2**), a large shift (4500  $\text{cm}^{-1}$ ) of the emission maxima ( $\lambda_{\text{em}}$ ) is observed when dioxane is replaced by DMSO. When increasing the solvent polarity, the curves area increases, reaches a maximum and then decreases. The associated fluorescence quantum yield ( $\Phi_f$ ) is over 30% on the range of solvents; the maximum value (57%) is obtained in butyronitrile ( $\epsilon = 20.3$ ). Similar results are obtained with **a1**.

The same evolution is observed for the cyano/dibutylamino end substituted compound (**c1**), but fluorescence strongly decreases with solvent polarity, and no more exists beyond dichloromethane ( $\epsilon = 8.93$ ). Concerning the fluorescence yield, the maximum (80%) is higher than for **a2** and reached for a very low polarity solvent (diethyl ether:  $\epsilon = 4.2$ ). Also the reduce polarity range of solvents is narrower ( $\Delta\epsilon$  of 7.56 and 44.24 for **c1** and **a2**, respectively), the shift is more important ( $>5000 \text{ cm}^{-1}$ ). The more important effect of solvent polarity on **c1** could result from a more efficient charges delocalization on the excited state, as expected with a stronger A/D pair.

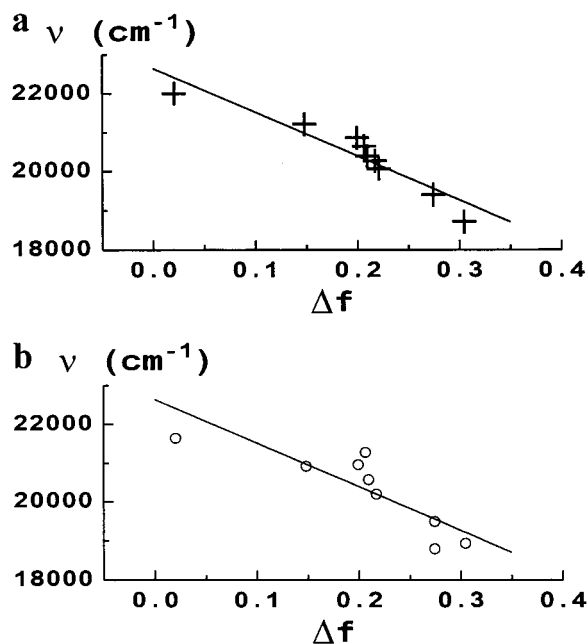
The large solvatochromic behavior observed for **a2** and **c1** is attributed to an intramolecular charge transfer (ICT) state involving charge separation within the whole molecule, inducing consequently a large dipole moment for the excited state. The gain in the molecular dipole moments induced by the photoexcitation could be calculated by plotting the position of the fluorescence maximum  $\nu_{\text{max}}$  vs Lippert's  $\Delta f$  function<sup>29</sup>

$$\nu_{\text{max}} = - \frac{2(\mu_e - \mu_g)^2}{hca^3} \left[ \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right] + Cste = - \frac{2(\mu_e - \mu_g)^2}{hca^3} \Delta f + Cste \quad (1)$$

where  $\mu_g$  and  $\mu_e$  refer to the dipole moments of ground and excited states of the molecule, respectively,  $h$  is Planck's constant,  $c$  is the velocity of light,  $a$  is the radius of Onsager cavity which fits the molecule, and  $\epsilon$  and  $n$  are the solvent dielectric constant and refractive index, respectively. As can be seen from Figure 3, parts a and b, a linear plot is obtained for compound **a1** and **a2**. A change of 15 D in dipole moment of **a1** between the ground state and the singlet excited state is deduced from the slope, the Onsager radius  $a$  being estimated by chemical modelization (see Experimental Section). This result confirms that the species formed in the excited state must have a different charge localization in comparison to that in the ground state. The same conclusion is also available for **a2**.

Unfortunately, such exploitation is not possible for **c1**, due to the too low available range of solvents.

**3.4. Nonlinear Optical Properties.** EFFISH<sup>25,26</sup> experiments were carried out in solutions of dichloromethane at 1.32  $\mu\text{m}$ . The values of the scalar product  $\mu\beta_{J=1}$ , where  $\beta_{J=1}$  is the vector part of the  $\beta$  tensor, were deduced from these experiments. In the following, we will write  $\beta_{J=1} \equiv \beta$  for clarity. The values of  $\mu\beta$ ,  $\mu\beta_0$ , and  $\beta_0$  (first hyperpolarizability extrapolated to infinite



**Figure 3.** Evolution of fluorescence maximum wavelength of **a1** (a) and **a2** (b) in solvents of different polarity as a function of Lipper's  $\Delta f$  parameter.

wavelength), as well as those of  $\lambda_{\max}$ , are reported in Table 2. The static  $\mu\beta_0$  values have been calculated according to the two-level model.<sup>30</sup> Disperse Red 1 (DR1) has been characterized for comparison.

The values of  $\mu\beta$  ( $\mu\beta_0$ ) lie between  $130 \times 10^{-48}$  and  $1480 \times 10^{-48}$  esu ( $80 \times 10^{-48}$  and  $775 \times 10^{-48}$  esu). The results do not evidence significant difference within series **a** whatever  $R_1$ , and series **b** whatever  $R_2$ . The lateral  $R_1$  and/or  $R_2$  substituents do not influence NLO properties.

On the contrary, the  $\mu\beta$  values are influenced by the nature of the end substituents. As expected, replacing weak electron withdrawing and donating groups (such as cyano and *n*-hexyloxy) by stronger ones (nitro and dibutylamino) enhances the  $\mu\beta_0$  values by a factor of 8 (from  $95 \times 10^{-48}$  for **a1** to  $775 \times 10^{-48}$  esu for **d1**). These results confirm that the 3,3'-bipyridine bridge is efficient and that the electron delocalization occurs.

In the case of the amino donor groups, the chemical structure can also influence the NLO efficiency:  $\mu\beta$  values are more important for the dibutylamino group than for the hexylpiperazino one, whatever the acceptor group (nitro or cyano) ( $1200 \times 10^{-48}$  and  $510 \times 10^{-48}$  esu for **c1** and **c\*2**, respectively;  $1480 \times 10^{-48}$  and  $765 \times 10^{-48}$  esu for **d1** and **d\*2**, respectively). These latter results confirm that hexyloxypiperazino is a less efficient donor group than dibutylamino, as ever seen with the linear optical data ( $\lambda_{\max}$ ).

Concerning the  $\beta_0$  values of the mesogenic chromophores we reported, they lie between  $16 \times 10^{-30}$  (**a2**) and  $(60\text{--}85) \times 10^{-30}$  esu (**d\*2**). The higher values are in the same order as those of the well-known isotropic dye DR1. Consequently, as far as we know from the literature,<sup>15–17,31–34</sup> it seems that **d\*2** exhibits a significant hyperpolarizability compared to typical mesogenic compounds active in NLO (see Table 3). In fact,  $\beta_0$

values for typical enantiotropic chromophores range from  $5 \times 10^{-30}$  to  $32 \times 10^{-30}$  esu. A  $\beta_{\text{HRS0}}$  value of  $114 \times 10^{-30}$  esu was reported for a pyrazoline derivative<sup>15</sup> which exhibits only a monotropic  $S_A$  phase at low temperature (C–I, 93.1 °C; I– $S_A$ , 71.4 °C).

**3.5. Relation between Photoluminescence and NLO Properties.** Oudar and Chemla<sup>28</sup> have shown that push–pull compounds having a low-lying high-intensity ICT transition (in absorption), associated with a large change in dipole moment, yield large quadratic hyperpolarizabilities ( $\beta_{\text{CT}}$ ). Using a two-level quantum mechanical model, the dominant component  $\beta_{\text{CT}}(0)$  can be written

$$\beta_{\text{CT}}(0) = \frac{3}{2} \frac{\hbar^2 e^2 (\mu_e - \mu_g)}{m W_0^3} f \quad (2)$$

where  $e$  and  $m$  are the charge and mass of the electron, and  $f$  and  $W_0$  are the oscillator strength and transition energy from the ground state to the first excited state, respectively. Paley et al.<sup>35</sup> have developed a solvatochromic method in order to calculate  $\beta_{\text{CT}}(0)$  from eq 2: the required value of the excited-state dipole moment,  $\mu_e$ , is obtained from a theoretical treatment of solvatochromism shift in absorption developed by McRae,<sup>36</sup> while  $W_0$ ,  $f$  are easily determined from UV–vis absorption spectrum of the molecule in solution, and  $\mu_g$  is deduced from analysis of the dielectric constant and refractive index for solutions at several concentrations.

In the case of the “push–pull” chromophores, we propose to perform a rough calculation of  $\beta_{\text{CT}}(0)$  in a simpler way, based on the solvatochromism of the emission band. To calculate  $\beta_{\text{CT}}(0)$  from eq 2,  $W_0$  and  $f$  are determined from the absorption band as previously, but the dipole moment change,  $\mu_e - \mu_g$ , is deduced from eq 1. The calculated  $\beta_{\text{CT}}(0)$  value for **a1** and **a2**, ca.  $(15\text{--}20) \times 10^{-30}$  esu, is consistent with the experimental  $\beta_{\text{CT}}(0)$  value determined by EFISHG measurements.

Unfortunately, the same treatment cannot be performed for **c1** and **c\*2** because  $\mu_e - \mu_g$  is not experimentally accessible (see section 3.3).

#### 4. Conclusion

In conclusion, we have synthesized a new class of NLO chromophores based on 6,6'-distyryl-3,3'-bipyridine resulting from the Knoevenagel condensation of the 3,3'-bipyridine core with differently substituted aromatic aldehydes.

The versatility of the chemical way allows us, by lateral substitution of the  $\pi$ -conjugated core and varying the end substituents, to tune mesogenic, linear optical and NLO properties of these push–pull molecules. In all cases, for a A/D pair, mesogenic compounds which exhibit significant  $\beta_0$  were obtained.

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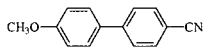
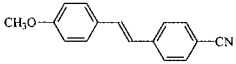
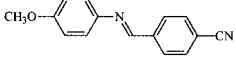
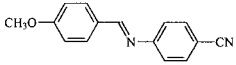
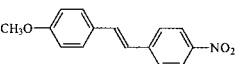
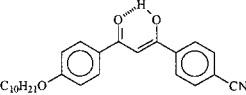
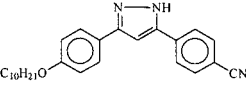
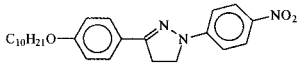
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**Table 3. Selected Linear (Absorption Maximum  $\lambda_{\text{Max}}$ ) and Nonlinear Optical Data ( $\beta$  and  $\beta_0$ ) of NLO Active Mesogenic Groups Reported in the Literature**

Compound	Absorption	NLO properties
	$\lambda_{\text{max}}$ (nm)	$\beta/\beta_0$ from literature
 29	292	$\beta = 17.10 \cdot 10^{-30}$ esu (at 1.06 $\mu\text{m}$ ) $\beta_0 = 11.10 \cdot 10^{-30}$ esu
 30	342	$\beta = 19.10 \cdot 10^{-30}$ esu (in DMSO at 1.9 $\mu\text{m}$ ) $\beta_0 = 15.10 \cdot 10^{-30}$ esu
 17	353	$\beta = 23 \pm 10.10 \cdot 10^{-30}$ esu (in acetone at 1.06 $\mu\text{m}$ ) $\beta_0 = 11 \pm 5.10 \cdot 10^{-30}$ esu
 17	317	$\beta = 16 \pm 30.10 \cdot 10^{-30}$ esu (in acetone at 1.06 $\mu\text{m}$ ) $\beta_0 = 9 \pm 5.10 \cdot 10^{-30}$ esu
 31	374	$\beta = 74.10 \cdot 10^{-30}$ esu (at 1.06 $\mu\text{m}$ ) $\beta_0 = 32.10 \cdot 10^{-30}$ esu
 16	363	$\beta = 12 \pm 3.10 \cdot 10^{-30}$ esu (in dioxane at 1.38 $\mu\text{m}$ ) $\beta_0 = 8 \pm 2.10 \cdot 10^{-30}$ esu
 16	276	$\beta = 6 \pm 2.10 \cdot 10^{-30}$ esu (in dioxane at 1.38 $\mu\text{m}$ ) $\beta_0 = 5 \pm 1.10 \cdot 10^{-30}$ esu
 a) 15	430 (CHCl <sub>3</sub> )	$\beta_{\text{HRS}} = 393.10 \cdot 10^{-30}$ esu $\beta_{0\text{HRS}} = 114.10 \cdot 10^{-30}$ esu

<sup>a</sup> This molecule presents only monotropic S<sub>A</sub> mesophases C–I (93.1 °C)–S<sub>A</sub> (71.4 °C).

In the case of amino compounds, there is a lowering in first hyperpolarizability when introducing bulk mesogenic properties with the hexylpiperazino group (**c\*2** and **d\*2** vs **c1** and **d1**, respectively).

In the case of the chromophores bearing a *n*-hexyloxy group, we managed to synthesize two homologous series (**a1**, **a2**, **a4** and **b2**, **b3**, **b4**). Within these series, there is almost constant hyperpolarizability, while the mesogenic properties are different.

Considering this latter series as model compounds, the use of benzaldehydes bearing reactive functional groups will offer the opportunity to synthesize reactive chromophores able to be grafted on macromolecular chain, with a view to obtain side chain polymers and SCLCPs exhibiting NLO properties. This approach would allow us to demonstrate the interest of using mesogenic chromophores, comparing the NLO properties of side chain liquid crystal polymers and of their non liquid crystal homologous polymer. This work is under investigation and will be described in a later paper.

Besides this, the photoluminescence, another property exhibited by most compounds, could be used to predict the NLO properties of fluorescent chromophores.

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**Supporting Information Available:** Text giving syntheses, <sup>1</sup>H and <sup>13</sup>C NMR data, and elemental analyses of mono-substituted and disubstituted compounds **b2**, **b3**, **b4**, **c1**, **c\*2**, **d1**, and **d\*2** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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