# New Octupolar Star-Shaped Strucures for Quadratic Nonlinear Optics

S. Brasselet,[†] F. Cherioux,[‡] P. Audebert,[§] and J. Zyss*[,†]

*LPQM, Ecole Normale Supérieure de Cachan, 61 Avenue du Président Wilson,*
*F-94235 Cachan, Cedex, France, Laboratoire de Chimie et Electrochimie Moléculaire,*
*Université de Franche-Comté, La Bouloie, 16 Route de Gray, F-25030, Besançon, Cedex,*
*France, and PPSM, Ecole Normale Supérieure de Cachan, 61 Avenue du Président Wilson,*
*F-94235 Cachan, Cedex, France*

*Received February 11, 1999. Revised Manuscript Received April 26, 1999*

Two new classes of octupolar nonlinear chromophores, deriving from 1,3,5-triazines and oligothienylic crystal violet analogues, have been synthesized and their nonlinear properties investigated using the harmonic light scattering experiment. The easy preparation of these molecules makes them attractive candidates for further applications. Off-resonant measurements show high nonlinearities together with an excellent transparency, which make these compounds of promising interest for the emerging schemes of nonlinear optical applications whereby the multipolar character of the chromophores is of particular importance.

## Introduction

Octupolar molecules have recently generated increasing interest in the field of quadratic nonlinear optics. At the microscopic level, strategies have been developed during the past decade in order to circumvent the eventual drawbacks of unidimensional and so-called dipolar molecules, for which a strong nonlinearity is often antagonized by a strong absorption at the visible harmonic wavelength. In particular, the large class of octupolar molecules belonging to the $T_d$, $D_{3h}$, or $C_{3v}$ symmetry groups has attracted the attention of both physicists and chemists since the early demonstrations that significant second-order nonlinear efficiency could be achieved from nondipolar molecules.[1,2] Octupolar molecular systems, due to their vanishing ground state dipole moment, consequently belong to a particular class of chromophores that are not amenable to traditional molecular nonlinear optics measurements that require electric field-induced orientation of the molecules in order to retrieve their hyperpolarizability coefficient, $\beta$. The revival of the earlier harmonic light scattering experiment introduced by Maker et al.,[3] performed in isotropic solutions and therefore adapted to such molecular systems,[4] has helped point out the particular interest of octupolar systems in terms of their favorably displaced nonlinearity−transparency tradeoff, opening therefrom new schemes in the field of molecular engineering for nonlinear optics.[5−8] This field has furthermore significantly gained interest since the first demonstration of the possibility to induce permanent macroscopic noncentrosymmetric order using octupolar molecules.[9] In this so-called "all optical poling" method, selective orientation of the chromophores in a solution or a polymer matrix is achieved by simultaneous irradiation of coherent IR-fundamental and visible-harmonic laser beams.[10] The orientation results from interference between multiphoton excitation pathways of the molecules and does not require any electric poling field as in traditional poling methods, which makes it suitable for any multipolar molecular compound. The possibility to design new symmetry schemes at the macroscopic level[11] has further triggered the design of nondipolar molecules and in particular of octupolar compounds such as those reported in this work.

We have recently reported the preparation and electrochemical properties of families of $D_{3h}$ conjugated molecules.[12] The first electrochemical results combined with theoretical calculations demonstrated $D_{3h}$ symmetry as well as extended electronic delocalization for in all compounds, thus pointing out their potentialities in the field of nonlinear optics. In this paper, we explore and confirm the nonlinear optical properties of these compounds. Nonlinear optical measurements were per-

---

[†] LPQM, Ecole Normale Supérieure de Cachan.

[‡] Université de Franche-Comté.

[§] PPSM, Ecole Normale Supérieure de Cachan.

(1) Joffre, M.; Yaron, D.; Silbey, R.; Zyss, J. *J. Chem. Phys.* **1992**, *97*, 5607.

(2) (a) Zyss, J. *Nonlinear Optics* **1991**, *1*, 3. (b) Zyss, J. *J. Chem. Phys.* **1993**, *98*, 6583. (c) Zyss, J.; Ledoux, I. *Chem. Rev.* **1994**, *94*, 77.

(3) (a) Terhune, R. W.; Maker, P. D.; Savage, C. M. *Phys. Rev. Lett.* **1965**, *14*, 681. (b) Maker, D. *Phys. Rev.* A **1970**, *1*, 923.

(4) (a) Clays, K.; Persoons, A. *Phys. Rev. Lett.* **1991**, *66*, 2980.

(5) Pauley, M. A.; Guan, H. W.; Wang, C. H.; Jen, A. K. Y. *J. Chem. Phys.* **1996**, *104*, 7821.

(6) Zyss, J.; Chauvan, T.; Dhenaut, C.; Ledoux, I. *Chem. Phys.* **1995**, *177*, 281.

(7) Dhenaut, C.; Ledoux, I.; Samuel, I. D. W.; Zyss, J.; Bourgault, M.; Le Bozec, H. *Lett. Nature* **1995**, *374*, 339.

(8) Fiorini, C.; Charra, F.; Nunzi, J. M.; Samuel, I. D. W.; Zyss, J. *Opt. Lett.* **1995**, *24*, 2469.

(9) (a) Verbiest, T.; Clays, K.; Persoons, A.; Meyers, F.; Bredas, J. L. *Opt. Lett.* **1993**, *7*, 525. (b) Stadler, S.; Feiner, F.; Brauchle, C.; Brandl, S.; Gompper, R. *Chem. Phys. Lett.* **1995**, *2−3*, 292.

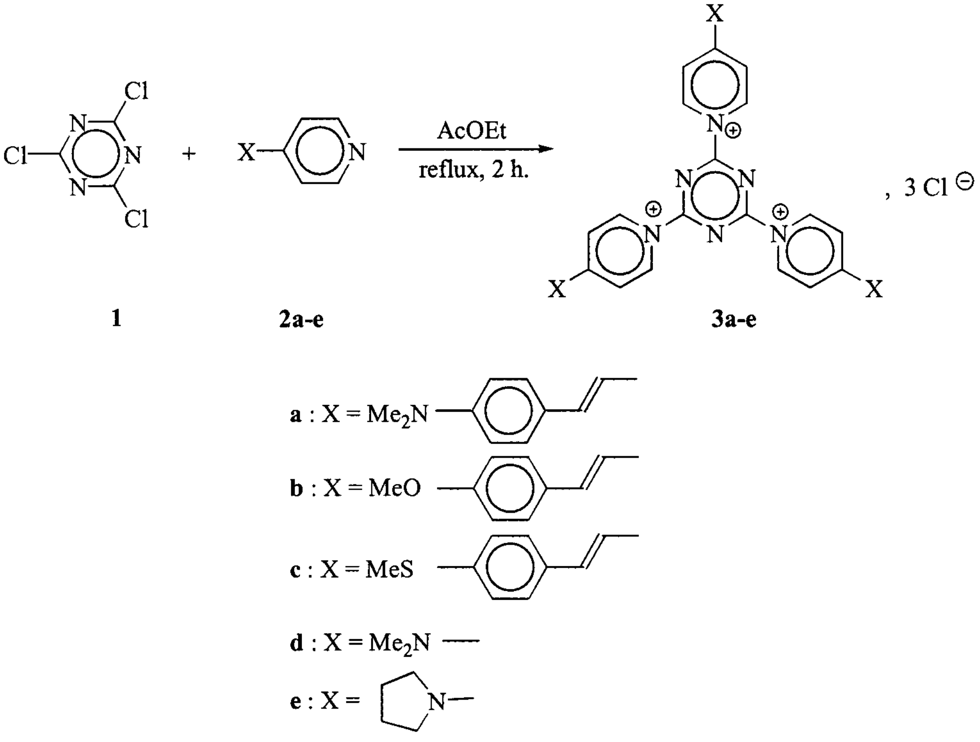
(10) (a) Fiorini, C.; Charra, F.; Nunzi, J. M. *J. Opt. Soc. Am. B* **1994**, *12*, 2347. (b) Nunzi, J. M.; Charra, F.; Fiorini, C.; Zyss, J. *Chem. Phys. Lett.* **1994**, *219*, 349.

(11) (a) Brasselet, S.; Zyss, J. *J. Opt. Soc. Am. B* **1998**, *1*, 257. (b) Brasselet, S.; Zyss, J. *Opt. Lett.* **1997**, *22*, 1464.

(12) (a) Cherioux, F.; Audebert, P.; Hapiot, P. *Chem. Mater.* **1998**, *7*, 1984. (b) Cherioux, F.; Guyard, L.; Audebert, P. *Adv. Mater.* **1998**, *13*, 1013.

10.1021/cm990093n CCC: $18.00

**Scheme 1. Synthesis of 2,4,6-tri-[1-Pyridinium]-1,3,5-triazine Trichloride 3**



formed using the harmonic light scattering experiment in off-resonance conditions, avoiding subsequently any eventual two-photon fluorescence background that frequently arises when working at the vicinity of the two-photon absorption band of the molecules.[13,14] After briefly recalling the synthetic procedure, we report off-resonant second harmonic generation measurements from two series, 1,3,5-triazines and oligothienylic crystal violet analogues, respectively.

## Results and Discussion

**Synthesis of the Molecules**. The trisubstituted (s)-triazines are easily made by aromatic nucleophilic substitution on cyanuric chloride **1** with the appropriate 4-styrylpyridines, **2a**–**e** (see Scheme 1). This type of reaction was soon investigated in the case of *N*,*N*-dimethylaminopyridine (DMAP) on an activated pyrimidine ring[15] or cyanuric chloride.[16] The nucleophilic character of the 4-styrylpyridines is comparable to standard pyridines bearing identical substituents. The original styrylpyridines used for the previous step were prepared from the classical aldolic condensation that occurs easily with good yields using the potassium *tert*-butoxide/DMF couple as base and solvent, respectively. This is an improved method as compared with previously described syntheses involving organometallic reagents.[17,18] The substitution took place smoothly within 2 h upon gentle warming with cyanuric chloride in ethyl acetate at room temperature to give the trisubstituted adduct **3a**–**e** as the sole product (see Scheme 1).

Beside the chloride counteranions directly arising from the synthesis, the trications have been prepared in association with iodide or hexafluorophosphate anions by exchange with the appropriate sodium or ammonium salt.

The tris(2-thienyl)methanol and tris(2-thienyl)methyl cation **5a** were synthesized by the method described in the literature.[19] The precursor carbinols **4b**–**c** are usually prepared by reaction of the corresponding 2-thienyllithium or 5-(2,2′-dithienyl)lithium with ethylchloroformate with a 3:1 stoichiometry (see Scheme 2). The tris(5-(2,2′:5′,2″-terthienyl)])methanol **4d** had be prepared in two steps with isolation of 5-ethyl-(2,2′:5′,2″-terthiophene)carboxylate (see Scheme 3). The tris[5-(oligothienyl)]methyl cations **5b**–**d** were produced by adding a stoichiometric amount of perchloric acid to a solution of the carbinols **4b**–**d** in dry acetonitrile (see Scheme 4). The perchlorate salt of the cation precipitates instantly as an intense deep blue or violet colored powder in a quantitative yield. In the case of tris(2-thienyl)methyl cation, the color of the salt is bright orange.

**Nonlinear Optics Measurements**. The octupolar geometric features of the molecules addressed in this work and the subsequent absence of a dipolar $\beta$ component rules out the application of the traditional EFISH technique,[20] based on a static electrical field poling scheme of molecules in solution, which leads to the sole dipolar component of the microscopic nonlinearity. The harmonic light scattering (HLS) experiment, first introduced by Terhune and Maker,[3a] is an alternative method to investigate multipolar molecules in

---

[13] Morrison, I. D.; Denning, R. G.; Laidlaw, W. M.; Stammers, M. A. *Rev. Sci. Instrum.* **1996**, *4*, 1445.

[14] Kaatz, P.; Sheldon, D. P. *Rev. Sci. Instrum.* **1996**, *4*, 1439.

[15] Schmidt, A.; Hetzheim, A. *Tetrahedron* **1997**, *53*, 1295.

[16] Katritzky, A. R.; Nowak-Wydra, B. *Chem. Scr.* **1984**, *24*, 7.

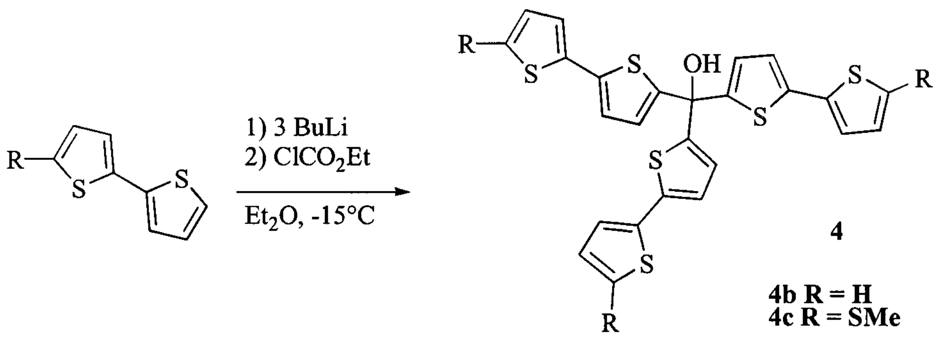
[17] Vasil'ev, A. N.; Mushkalo, L. K. *Zh. Obshch. Khim.* **1992**, *68*, 2087.

[18] Peesapati, V.; Rao, U. N.; Petrick, R. A. *J. Indian Chem. Soc.* **1991**, *68*, 3897.

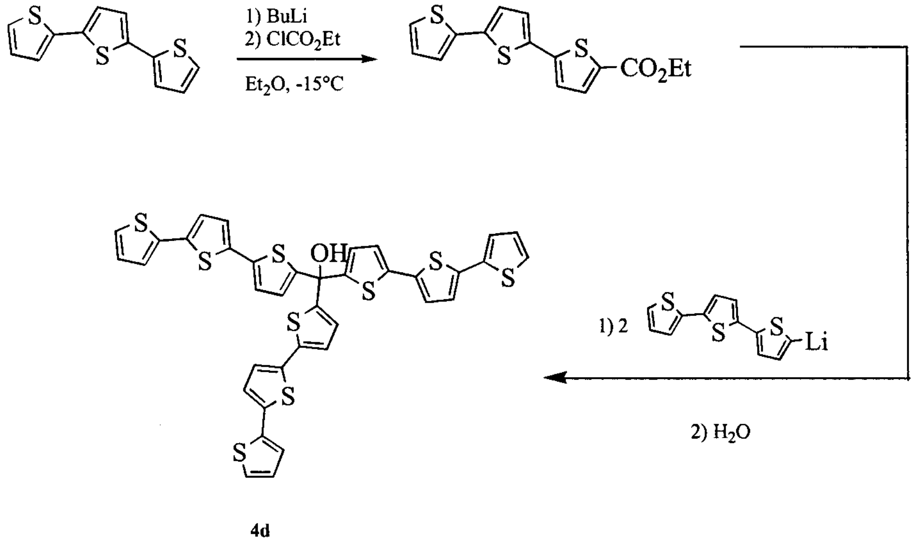
[19] Abarca, B.; Asensio, G.; Ballesteros, R.; Varea, T. *J. Org. Chem.* **1991**, *56*, 3224.

[20] Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664.

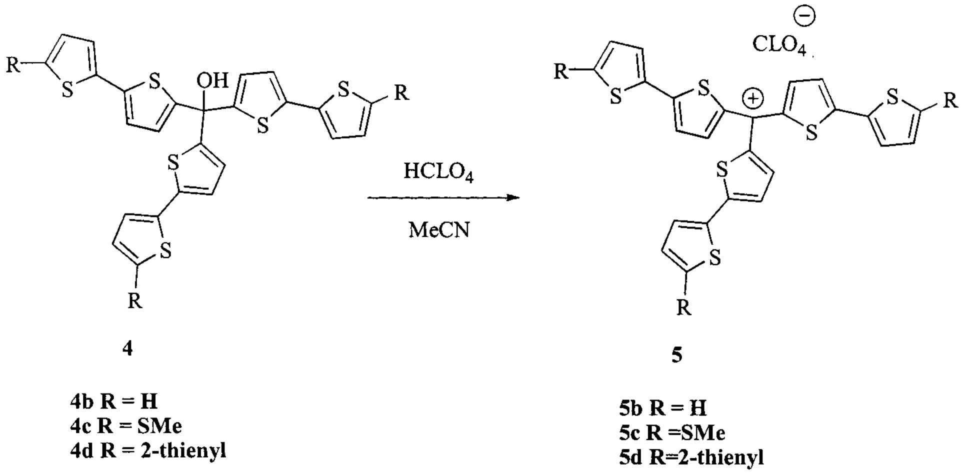
**Scheme 2. Synthesis of Tris[5-(oligothienyl)]methanol 4b−c.**



**Scheme 3. Synthesis of Tris[5-(2,2′:5′,2″-terthienyl)]methanol 4d.**



**Scheme 4. Synthesis of Tris[5-(oligothienyl)]methyl cations 5b-d.**



general, allowing for the determination of hyperpolarizabilities of nonpolar and/or ionic species based on the analysis of the noncoherent scattered second harmonic emission from an isotropic medium. Several studies have revived this experiment in view of molecular engineering studies addressing different molecular structures that are not amenable to EFISH, such as octupolar $D_{3h}$ molecules that are deprived of ground-state dipolar moment.[5−8,21]

As a result of the incoherent nature of the HLS process, the scattered nonlinear intensity $I^{2\omega}$ can be expressed as $I^{2\omega} = G(N_1\langle\beta_1^2\rangle + N_2\langle\beta_2^2\rangle)(I^{\omega})^2$ for a solution with $N_2$ (respectively, $N_1$) molecules/cm$^3$ of solute (respectively, solvent) where the $G$ coefficient embodies geometrical factors and experimental correction terms and the braces refer to statistical isotropic orientational averaging. A reference CCl$_4$ solution with $\sqrt{\langle\beta^2\rangle} = 0.26 \times 10^{-30}$ esu[3a] is used to calibrate the experiment. The $\sqrt{\langle\beta^2\rangle}$ value of the different molecules of interest can be inferred from the determination of the linear depen-

---

(21) Blanchard-Desce, M.; Baudin, J. B.; Ruel, O.; Jullien, L.; Brasselet, S.; Zyss, J. *Opt. Mater.* **1998**, *9*, 276.

**Table 1. Experimental Values of the $\sqrt{\langle\beta^2\rangle}$ Nonlinear Coefficient of 3a−e As Obtained by the Harmonic Light Scattering Measurement Performed at $\lambda = 1.34\ \mu$m in DMSO and Corresponding $\sqrt{\langle\beta^2\rangle}(0)$ Static Values after Dispersion by a Degenerate Two-Level Model (*1*)**

| compd | $\lambda_{\max}$ (nm) | $\sqrt{\langle\beta^2\rangle}$ ($10^{-30}$ esu) | $\sqrt{\langle\beta^2\rangle}(0)$ ($10^{-30}$ esu) |
|---|---|---|---|
| **3a** | 547 | fluorescence | |
| **3b** | 440 | 18.5 | 9.4 |
| **3c** | 470 | 45.6 | 20.3 |
| **3d** | 432 | 14.5 | 7.6 |
| **3e** | 310 | 11 | 8.2 |

**Table 2. Experimental Values of the $\sqrt{\langle\beta^2\rangle}$ Nonlinear Coefficient of 5a−d As Obtained by the Harmonic Light Scattering Measurement Performed at $\lambda = 1.34\ \mu$m in DMSO and Corresponding $\sqrt{\langle\beta^2\rangle}(0)$ Static Values after Dispersion by a Degenerate Two-Level Model (*1*)**

| compd | $\lambda_{\max}$ (nm) | $\sqrt{\langle\beta^2\rangle}$ ($10^{-30}$ esu) | $\sqrt{\langle\beta^2\rangle}(0)$ ($10^{-30}$ esu) |
|---|---|---|---|
| **5a** | 360 | 17.4 | 11.8 |
| **5b** | 350 | 20.5 | 14.3 |
| **5c** | 370 | 22.7 | 15 |
| **5d** | 360 | 45 | 29.7 |

dence of the harmonic intensity as a function of the square of the $I^{\omega}$ fundamental intensity at different molecular concentrations. An initial series of measurements addresses the pure solvent, namely, dimethyl sulfoxide (DMSO), with subsequent results further introduced in the analysis of the solution data. Typical concentration values are around $10^{-4}$ mol/L.

The fundamental IR laser source at 1.34 $\mu$m, allowing to red shift the second harmonic signal into the transparency region of all the molecules of interest, is a transverse and longitudinal single-mode flash pumped $Nd^{3+}$:Yag laser emitting pulses of 10 MW peak power and 10 ns duration at 10 Hz repetition rate. The incident intensity $I^{\omega}$ is monitored by a half-wave plate and a Glan polarizer. A fraction of the incident beam is removed by a glass plate at a small reflection angle and sent onto a reference NPP frequency doubling calibrated powder. The fundamental beam is focused in a cell, which contains the adequately filtered solutions. The scattered harmonic signal is then collected at a right angle on a second photomultiplier after spectral selection through an interference filter with 10 nm spectral resolution. Measurement of the solvent nonlinearity results in a nonlinear coefficient value of $\sqrt{\langle\beta^2\rangle} = 0.23 \times 10^{-30}$ esu.[21]

The nonlinear $\sqrt{\langle\beta^2\rangle}$ coefficients of the 1,3,5-triazine trichloride compounds, namely, **3a**−**e**, are given in Table 1 together with their $\lambda_{\max}$ absorption wavelength. The corresponding $\sqrt{\langle\beta^2\rangle}(0)$ static values were derived from a degenerate two-level dispersion model.[1]

Particular precautions were taken for those compounds with an absorption band coming close to the second harmonic wavelength. In particular, a two-photon fluorescence background may arise if the second harmonic wavelength, namely, 670 nm, lies at the edge of the absorption band of the molecular species.[13,14] In the case of **3a**, detection of the HLS signal at several distinct wavelengths around 670 nm performed by use of different interference filters evidenced that the harmonic wavelength signal was buried within a broad two-photon emission peak around 650 nm. The actual spectral resolution of the present detection setup did not permit discrimination of the HLS signal from the two-photon fluorescence background, and further development of this experiment is in progress in order to work at much higher incident fundamental wavelengths.

Compounds **3b**−**e** were studied using the same precautions and did not present any two-photon fluorescence background. The nonlinearity of **3b**, **3d,** and **3e** are slightly higher than the classical *p*-nitroaniline molecule, with $\sqrt{\langle\beta^2\rangle}(0) = 5 \times 10^{-30}$ esu as measured in chloroform in similar experimental conditions. The highest value was obtained for **3c**, which can be readily accounted for by a more favorable charge-transfer ensured by the stronger donor end group.

The nonlinear $\sqrt{\langle\beta^2\rangle}$ values of the tris[5-(oligothienyl)]methyl cations **5a**−**d** are given in Table 2. Comparison between the **5a**, **5b**, and **5d** values exemplifies the strong enhancement of the charge-transfer efficiency provided by the extension of the thienylic chains. The relatively higher efficiency obtained for **5d** while maintaining an excellent transparency in the visible range points out its particular relevance in terms of nonlinear−transparency tradeoff. Despite the poor donor strength of the end group of the three branches of this octupolar compound, the nonlinear efficiency of **5d** is significant and might be further improved by adequate grafting of donor groups.

The nonlinear values of the different compounds of this work are lower than those obtained for the well-known crystal violet carbocation for which $\sqrt{\langle\beta^2\rangle}(0) = 168 \times 10^{-30}$ esu.[22] The crystal violet compound has however a higher absorption wavelength, a situation potentially leading to contamination of the HLS signal by two-photon fluorescence.[22] A high absorption in the visible range is moreover detrimental for applications related to the second harmonic generation and parametric emission.

Molecules **3a**−**c** are furthermore good candidates for molecular engineering of macroscopic orientation of octupoles via the all-optical poling experiment.[9,10] A first demonstration of the orientation of the ethyl violet octupolar molecule has been already performed under strongly resonant conditions[9] and opened new possibilities in terms of engineering the symmetry of the macroscopic order provided by the orientation of multipolar molecules.[11] While presenting promising nonlinear efficiencies, octupolar compounds studied in this work present the advantage of a weaker absorption in the visible range, which would decrease the attenuation of interactive waves in the material.

## Experimental Section

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker-Spectrospin AC 200 spectrometer in DMSO-$d_6$ (except for carbinol **4** solvent: $CDCl_3$). 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, cyanuric chloride, 2,2′-bithiophene, 2,2′:

---

(22) Chui, T. W.; Wong, K. Y. *Chem. Phys. Lett.* **1996**, *4*, 1439.

5′,2″-terthiophene, and *n*-butyllithium were Acros or Aldrich products and were used without further purification. All experiments were made under nitrogen atmosphere, and solvents were freshly distilled prior to use.

**Synthesis of 4-Styrylpyridine 2a−c.** *General Procedure (See Scheme 1).* A mixture of 10 mmol of 4-picoline, 12 mmol of potassium *tert*-butoxide, and 10 mmol of aromatic aldehyde (respectively, 4-dimethylaminobenzaldehyde, 4-methoxybenzaldehyde, and 4-methylthiobenzaldehyde) is introduced in 50 mL of anhydrous DMF and heated 2 h at 80 °C under efficient magnetic stirring. After being cooled at room temperature, the mixture is 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 is separated, dried on sodium sulfate, and evaporated. The crude solid is recrystallized in the appropriated solvent.

**Spectroscopic Data for 2a−c.** *4-[4-(Dimethylamino)styryl]-pyridine **2a**.* Yield: 92% (recrystallization in toluene). F: 245−46 °C; lit 245−47 °C. $^1$H NMR: $\delta = 3.00$ ppm (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 (d, $J = 6.09$ Hz, 2H). $^{13}$C NRM: $\delta = 40.28$, 112.20, 117.93, 122.07, 122.89, 130.18, 140.60, 141.62, 151.76, 154.92 ppm.

*4-[4-(Methoxy)styryl]pyridine **2b**.* Yield: 94.8% (recrystallization in cyclohexane). F: 95 °C; lit 95 °C. $^1$H NMR: $\delta = 3.82$ ppm (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 (d, $J = 5.92$ Hz, 2H).$^{13}$C NRM: $\delta = 55.58$, 114.39, 120.69, 123.58, 128.65, 128.84, 132.75, 144.71, 150.04, 159.82 ppm.

*4-[4-(Methylthio)styryl]pyridine **2c**.* Yield: 90% (recrystallization in cyclohexane). F: 118−20 °C. $^1$H NMR: $\delta = 2.55$ ppm (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 (d, $J = 6.09$ Hz, 2H).$^{13}$C NMR: $\delta = 14.49$, 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 3**. *General Procedure (See Scheme 1).* 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**) into 50 mL of anhydrous ethyl acetate is added to 1.67 mmol of cyanuric chloride in 10 mL of the same solvent. The solid precipitate is recovered and washed three times with 50 mL of anhydrous acetone and dried in a vacuum to give the trications. All melting points are above 300 °C.

**Spectroscopic Data for 3.** *2,4,6-Tri[1-[4-[4-(dimethylamino)styryl]pyridinium]]-1,3,5-triazine Trichloride, **3a**.* Yield: 1.35 g (94.7%); mp >300 °C. $^1$H NMR: $\delta = 3.05$ ppm (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 (d, $J = 4.1$ Hz, 6H).$^{13}$C NMR: $\delta = 40.69$, 117.02, 121.20, 122.68, 131.73, 138.15, 138.35, 150.07, 152.81, 158.38, 162.44 ppm. Anal. Calcd for $C_{48}H_{48}Cl_3N_9{\cdot}5H_2O$: 60.85% C, 6.17% H, 13.31% N. Found: 60.97% C, 6.27% H, 13.26% N. $\lambda_{max} = 547$ nm.

*2,4,6-Tri[1-[4-[4-(methoxy)styryl]pyridinium]]-1,3,5-triazine Trichloride, **3b**.*Yield: 1.32 g (97.4%); mp >300 °C. $^1$H NMR: $\delta = 4.05$ ppm (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 (d, $J = 5.92$ Hz, 6H). $^{13}$C NMR: $\delta = 55.63$, 114.84, 121.08, 122.51, 130.78, 131.07, 157.44, 158.53, 156.62, 161.83, 162.80 ppm. Anal. Calcd for $C_{45}H_{39}N_6Cl_3O_3{\cdot}5H_2O$: 59.50% C, 5.44% H, 9.25% N. Found: 59.66% C, 5.64% H, 9.21% N. $\lambda_{max} = 440$ nm.

*2,4,6-Tri[1-[4-[4-(thiomethyl)styryl]pyridinium]]-1,3,5-triazine Trichloride, **3c**.* Yield: 1.40 g (97.5%); mp >300 °C. $^1$H NMR: $\delta = 2.56$ ppm (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 (d, $J = 6.08$ Hz, 6H).$^{13}$C NMR: $\delta = 14.19$, 123.26, 129.32, 138.33, 143.15, 143.42, 149.15, 157.12, 158.26, 159.57, 162.65 ppm. Anal. Calcd for $C_{45}H_{39}N_6Cl_3S_3{\cdot}5H_2O$: 56.51% C, 5.16% H, 8.79% N. Found: 56.65% C, 5.28% H, 8.74% N. $\lambda_{max} = 470$ nm.

*2,4,6-Tri[1-[4-dimethylaminopyridinium]]-1,3,5-triazine Trichloride, **3d**.* Yield: 0.97 g (95%); mp >300 °C. $^1$H NMR: $\delta = 3.22$ ppm (s, 18H, NMe$_2$), 7.05 (d, $J = 7.53$ Hz, 6H), 8.25 (d, $J = 7.63$ Hz, 6H). $^{13}$C NMR: $\delta = 40.69$, 107.49, 136.75, 157.03, 162.27 ppm. Anal. Calcd. for $C_{24}H_{30}Cl_3N_9{\cdot}5H_2O$: 44.97% C, 6.29% H, 19.66% N. Found: 45.10% C, 6.64% H, 19.58% N. $\lambda_{max} = 432$ nm.

*2,4,6-Tri[1-[4-pyrrolidinopyridinium]]-1,3,5-triazine Trichloride, **3e**.* Yield: 1.00 g (95.6%); mp >300 °C. $^1$H NMR: $\delta = 2.07$ 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 (d, $J = 7.86$ Hz, 6H).$^{13}$C NMR: $\delta = 27.71$, 49.35, 108.15, 136.67, 155.06, 162.12 ppm. Anal. Calcd. for $C_{24}H_{36}Cl_3N_9{\cdot}5H_2O$: 44.55% C, 7.16% H, 19.48% N. Found: 44.76% C, 7.36% H, 19.44% N. $\lambda_{max} = 310$ nm.

**Synthesis of Carbinols 4b−c.** *General Procedure (See Scheme 2).* To a solution of 2,2′-bithiophene or 5-alkylthio-2,2′-bithiophene (5.0 mmol) in 20 mL of dry ether was added *n*-butyllithium (5.0 mmol, 3.12 mL of 1.6 M solution in hexanes) at −15 °C. The solution was stirred 1 h, and ethyl chloroformate (1.66 mmol) was added. After 2 h of stirring, the solution was hydrolyzed with an aqueous saturated sodium hydrogen carbonate solution and extracted with ether. The organic layer was dried over $Na_2SO_4$ and evaporated. The crude product was separated on a silica column (dichloromethane:petroleum ether (1:1)). Yield: 60%.

**Spectroscopic Data for Carbinols 4b−c.** *Tris(5-(2,2′-dithienyl))methanol, **4b**.* $^1$H NMR: $\delta = 6.96$ ppm (d, 3H, $J = 3.8$ Hz, H$^4$), 7.07 ppm (dd, 3H, $J = 3.5$ Hz and $J = 5.1$ Hz, H$^{4'}$), 7.17 ppm (d, 3H, $J = 3.7$ Hz, H$^3$), 7.29 ppm (dd, 3H, $J = 1.1$ Hz and $J = 3.5$ Hz, H$^{3'}$), 7.49 ppm (dd, 3H, $J = 1.1$ Hz and $J = 5.1$ Hz, H$^{5'}$), 7.77 ppm (s, 1H, OH). $^{13}$C NMR: $\delta = 74.6$, 123.4, 124.1, 125.6, 126.8, 128.4, 136.4, 136.45, 150.4 ppm. HRMS (*m/z*): M$^{\bullet+}$ 524. IR: $\bar{\nu}$(OH) = 3497 cm$^{-1}$.

*Tris(5-[5′-methylthio-(2,2′-dithienyl)])methanol, **4c**.* $^1$H NMR: $\delta = 2.50$ ppm (s, 9H, SCH$_3$), 3.30 ppm (s, 1H, OH), 6.94 ppm (d, 3H, $J = 3.7$ Hz, H$^4$), 6.95 ppm (d, 3H, $J = 3.7$ Hz, H$^{4'}$), 6.98 ppm (d, 3H, $J = 3.7$ Hz, H$^3$), 6.99 ppm (d, 3H, $J = 3.7$ Hz, H$^{3'}$). $^{13}$C NMR: $\delta = 21.9$, 75.9, 122.9, 123.9, 127.0, 131.5, 137.7, 138.8, 148.8 ppm. HRMS (*m/z*): M$^{\bullet+}$ 662. IR: $\bar{\nu}$(OH) = 3480 cm$^{-1}$.

**Synthesis of 5-Ethyl-(2,2′:5′,2″-terthiophene)carboxylate.** To a solution of 2,2′:5′,2″-terthiophene (0.80 mmol, 200 mg) in 5 mL of dry ether was added *n*-butyllithium (0.80 mmol, 0.50 mL of 1.6 M solution in hexanes) at −15 °C. The solution was stirred 2 h at this temperature, and ethyl chloroformate (0.80 mmol) was added. The stirring was continued for 24 h. The solution was hydrolyzed with 20 mL of a aqueous saturated sodium hydrogen carbonate solution and extracted with 15 mL of ether. The organic layer was dried over $Na_2SO_4$ and evaporated. The crude product was separated on a silica column (dichloromethane:petroleum ether (1:1)). Yield: 25%.

**Spectroscopic Data for 5-Ethyl-(2,2′:5′,2″-terthiophene)-carboxylate.** $^1$H NMR in CDCl$_3$: $\delta = 1.39$ ppm (t, 3H, $J = 7.2$ Hz, -CH$_2$-*CH$_3$*), 4.37 ppm (q, 2H, $J = 7.2$ Hz O-*CH$_2$*-CH$_3$), 7.14 ppm (m, 6H, H$^3$, H,$^4$ H$^{3'}$, H$^{4'}$, H$^{3''}$, H$^{4''}$), 7.71 ppm (d, 1H, H$^{5''}$).

**Synthesis of Tris(5-(2,2′:5′,2″-terthienyl)])methanol, 4d.** To a solution of 2,2′:5′,2″-terthiophene (0.36 mmol, 90 mg) in 3 mL of dry ether was added *n*-butyllithium (0.36 mmol, 0.025 mL of 1.6 M solution in hexanes) at −15 °C. The solution was stirred 1H30 and 5-ethyl-(2,2′:5′,2″-terthiophene)carboxylate (0.18 mmol, 30 mg) was added. The stirring was continued for 30 min, and the solution was hydrolyzed with 10 mL of an aqueous saturated sodium hydrogen carbonate solution and extracted with ether. The organic layer was dried over $Na_2SO_4$ and evaporated. The residue was stirred 2 h in dichloromethane at −15 °C. The precipitated solid was filtered and dried under vacuum. Yield: 50%.

**Spectroscopic Data for Tris(5-(2,2′:5′,2″-terthienyl)])-methanol, 4d.** $^1$H NMR: $\delta = 7.05$ ppm (d, 3H, $J = 3.9$ Hz, H$^4$), 7,15 ppm (dd, 6H, $J = 3.7$ Hz and $J = 5$ Hz, H$^{4''}$), 7.27 ppm (d, 3H, $J = 3.9$ Hz, H$^3$), 7.31 ppm (s, 6H, H$^{3'}$ and H$^{4'}$), 7.39 ppm (dd, 3H, $J = 0.7$ Hz and $J = 3.5$ Hz, $H^{3''}$), 7.58 ppm (dd, 3H, $J = 0.7$ Hz and $J = 5$ Hz, $H^{5''}$), 7.84 ppm (s, 1H, OH). $^{13}$C NMR: $\delta = 74.8$, 123.8, 124.4, 125.1, 125.9, 127.0, 128.6, 135.1, 135.6, 136.0, 150.6 ppm. HRMS ($m/z$): $M^{\bullet +}$ 770. IR: $\bar{\nu}$(OH) = 3490 cm$^{-1}$.

**Synthesis of Tris[5-(oligothienyl)]methyl Cations 5b−d.** *General Procedure (See Scheme 4).* To a solution of carbinol **4** (50 mg) in 10 mL of dry acetonitrile was added 2 mL of perchloric acid. The solution was stirred 15 min, and 5 mL of dry ether was added. The solid obtained was filtered under vacuum and washed with dry ether (quantitative yield). All melting points are above 300 °C.

**Spectroscopic Data of Tris(5-oligothienyl)methyl Cations 5b−d.** *Tris[5-(2,2′-dithienyl)]methyl Cation, **5b**.* $^1$H NMR: $\delta = 7.01$ ppm (3H, d, $J_{H3-H4} = 3.8$ Hz, $H^4$), 7.13 ppm (3H, dd, $J_{H3'-H4'} = 3.6$ Hz and $J_{H4'-H5'} = 5.1$ Hz, $H^{4'}$), 7.23 ppm (3H, d, $J_{H3-H4} = 3.8$ Hz, $H^3$), 7.35 ppm (3H, dd, $J_{H3'-H5'} = 1.2$ Hz and $J_{H3'-H4'} = 3.6$ Hz, $H^{3'}$), 7.56 ppm (3H, dd, $J_{H3'-H5'} = 1.2$ Hz and $J_{H4'-H5'} = 5.1$ Hz, $H^{5'}$). $^{13}$C NMR: $\delta = 123.4$, 124.1, 125.6, 126.7, 128.4, 136.3, 136.4, 136.5, 150.4 ppm. HRMS ($m/z$): $M^{\bullet +} = 506$ (without counterion). $\lambda_{max}$ (DMSO) = 350 nm.

*Tris[5′-(5-thiomethyl-2,2′-dithienyl)]methyl Cation, **5c**.* $^1$H NMR: $\delta = 2.70$ ppm (9H, s, S−CH$_3$), 6.92 ppm (3H, d, $J_{H3-H4} = 3,7$ Hz, $H^4$), 7.04 ppm (3H, d, $J_{H3'-H4'} = 3,7$ Hz, $H^{4'}$), 7.12 ppm (3H, d, $J_{H3-H4} = 3,7$ Hz, $H^3$), 7.16 ppm (3H, d, $J_{H3'-H4'} = 3,7$ Hz, $H^{3'}$). $^{13}$C NMR: $\delta = 20.8$, 123.5, 124.5, 126.8, 128.9, 131.2, 135.8, 136.2, 137.6, 150.5 ppm. HRMS ($m/z$): $M^{\bullet +} = 644$ (without counterion). $\lambda_{max}$ (DMSO) = 370 nm.

*Tris[5-(2,2′:5′,2″-terthienyl)]methyl Cation, **5d**.* $^1$H NMR: $\delta = 7.25$ ppm (3H, d, $J_{H3-H4} = 3.9$ Hz, $H^4$), 7.29 ppm (6H, dd, $J_{H3''-H4''} = 3.7$ Hz and $J_{H4''-H5''} = 5.0$ Hz, $H^{4''}$), 7.42 ppm (3H, d, $J_{H3-H4} = 3.9$ Hz, $H^3$), 7.53 ppm (6H, s, $H^{3'}$ et $H^{4'}$), 7.58 ppm (3H, dd, $J_{H3''-H5''} = 0.7$ Hz and $J_{H3''-H4''} = 3.7$ Hz, $H^{3''}$), 7.79 ppm (3H, dd, $J_{H3''-H5''} = 0.7$ Hz and $J_{H4''-H5''} = 5.0$ Hz, $H^{5''}$). $^{13}$C NMR: $\delta =$123.8, 124.4, 125.1, 125.9, 127.0, 128.7, 135.2, 135.6, 136.0, 150.6 ppm. HRMS ($m/z$): $M^{\bullet +} = 752$ (without counterion). $\lambda_{max}$ (DMSO) = 350 nm.

## Conclusion

The molecular engineering of 1,3,5-triazines and oligothienylic crystal violet analogues has been presented as a promising approach to octupolar compounds for nonlinear optics. High off-resonant second-order nonlinear coefficient have been reported in the case of the oligothienylic compounds, while the chemical structure of both families of molecules is of a particular interest for future applications related to optical orientation in polymer matrixes. These results, calling for further optimization of the molecular structure and in particular of the donor and acceptor groups, already confirm the relevance of these new octupolar compounds in the field of multipolar nonlinear optics.

CM990093N