ChemComm

Synthesis and characterisation of an octupolar polymer and new molecular octupoles with off-resonant third order optical nonlinearities

Frédéric Chérioux,*[a] Hervé Maillotte,[b] Pierre Audebert[a]† and Joseph Zyss[c]

[a] *Laboratoire de Chimie et Electrochimie Moléculaire, UFR Sciences et Techniques, 16 route de Gray, F-25030 Besancon cedex, France. E-mail: frederic.cherioux@univ-fcomte.fr*

[b] *Laboratoire d'Optique P.M. Duffieux, Unité Mixte de Recherche CNRS/Université de Franche-Comté no 6603, Institut des Microtechniques de Franche-Comté, UFR Sciences et Techniques, 16 route de Gray, F-25030 Besancon cedex, France.*

[c] *Laboratoire de Photonique Quantique et Moléculaire, Unité Mixte de Recherche CNRS no 8537, Ecole Normale Supérieure, 61 Avenue du Président Wilson, F-94235 Cachan cedex, France*

Received (in Cambridge, UK) 21st July 1999, Accepted 10th September 1999

The first synthesis and Z-scan measurements of an octupolar polymer with off-resonant third order nonlinear optical properties are discussed; two other new molecular thiophene-based octupoles with similar nonlinearities are also reported.

In the quest for materials suitable for electro-optical and all-optical devices,[1] the last decade has witnessed considerable interest in the quadratic nonlinear optical (NLO) properties of organic or organometallic octupolar molecules.[2] Such octupolar compounds with multi-directional charge-transfer transitions enlarge the scope of molecular engineering for nonlinear optics,[3] previously restricted to dipolar compounds with single-directional charge-transfer transitions. Improving the NLO efficiency/transparency (or figure-of-merit) trade-off stands out among the important goals of this approach. Indeed, the particular symmetry of octupoles may lead to a better transparency and improved stability compared with classical dipoles,[2] although the question has not been completely elucidated as yet.[4] Besides, all-optical poling, which does not require a permanent dipole, has been shown to allow for noncentrosymmetric statistical macroscopic orientation.[2]

In all-optical applications based on the optical Kerr effect, it is also of paramount importance to improve the figures-of-merit[5] (recalled below) of cubic NLO materials because high nonlinear refractive indices in dipolar organics are generally obtained *via* resonant enhancement, at the expense of large linear or nonlinear absorption losses. However, only a small number of studies have reported cubic NLO properties of octupolar compounds. Large nonlinear refractive indices have been effectively measured in only two recent works, one dealing with organic octupolar molecules[6] and the second with organometallic octupolar complexes.[7] But in both cases, resonant enhancement of the nonlinear refractive index occurred, resulting from, respectively, three- or two-photon dispersion effects associated with absorption losses.

Moreover, to the best of our knowledge, no synthesis of octupolar polymers having NLO properties has so far been reported in the literature in spite of their potential interest towards further material and device investigations.

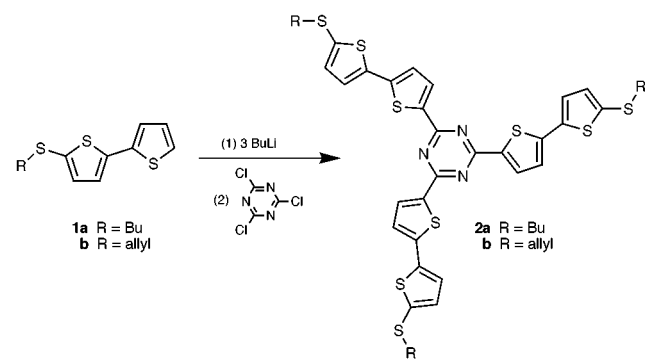
We report here the first efficient synthesis of an octupolar polymer {poly[2,4,6-tris(5′-(5-allylthio-2,2′-bithienyl-5-yl)-1,3,5-triazine]} as well as two new molecular octupoles [2,4,6-tris(5′-alkylthio-2,2′-bithienyl-5-yl)-1,3,5-triazine] which exhibit large non-resonant nonlinear refractive indices. The synthesis, UV-visible spectroscopy and Z-scan measurements of these three compounds are presented and their figures-of-merit are also discussed.

† Present Address: PPSM-Département de Chimie, Unité Mixte de Recherche CNRS n°8531, Ecole Normale Supérieure, 61 Avenue du Président Wilson, F-94235 CACHAN cedex, France.

We chose 5-*n*-butylthio-2,2′-bithiophene **1a** and 5-allylthio-2,2′-bithiophene **1b** as precursors in view of the two following assets: (i) the *n*-butyl chain of **1a** helps to increase the solubility of final molecule **2a**, and (ii) the allylthio function of **1b** can be easily homopolymerised using AIBN as a radical initiator.[8]

These two precursors **1a**,**b** were synthesised following Hill *et al.*[9] All products were purified by column chromatography with light petroleum–CH_2Cl_2 (1 : 1) as eluent. According to our earlier method,[10] octupoles **2a**,**b** were synthesised *via* a triple aromatic nucleophilic substitution of 3 equiv. of 5′-alkylthio-2,2′-bithienyl-5-yllithium salt on cyanuric chloride (see Scheme 1). Such reactions are efficient, with yields as high as 90%. The trisubstituted products **2a**,**b**‡ were only isolated because such reactions are activated by the mesomer attractive power of the three nitrogen atoms of cyanuric chloride. This electronic property stabilises the intermediate species of the aromatic nucleophile substitution. Octupoles **2** display D_{3h} symmetry. These molecules are completely planar in the absence of steric hindrance around the 1,3,5-triazine centre. Such symmetry has been confirmed by *ab initio* and semi-empirical computations as well as by electrochemical characterisation in the case of similar octupolar molecules.[11]

The new polymer **3** was synthesised in quantitative yield by radical homopolymerisation of octupolar monomer **2b** with AIBN as radical precursor (see Scheme 2). In order to obtain the pure polymer only, the reaction was continued until monomer **2b** was no longer detectable by thin layer chromatography. The crude polymer was then precipitated in Et_2O to obtain pure polymer **3**‡ as an orange–yellow powder. The octupolar character of monomer **2b** is retained during its homopolymerisation because the monomer is based on a very rigid sp^2 skeleton. All products **2** and **3** are very soluble in toluene at concentrations close to 0.1 mol l^{-1}. Also, THF is a good solvent. The polymer was analysed by SEC (THF solution, evaluation by comparison with a polystyrene standard) giving M_n = 1970 g mol^{-1}, M_w = 4800 g mol^{-1} and polydispersity =



Scheme 1

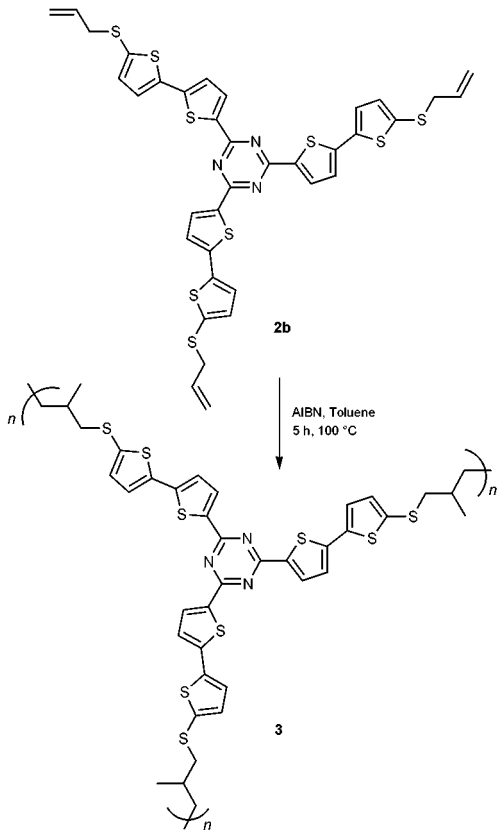
This journal is © The Royal Society of Chemistry 1999

2.43. Therefore, from SEC analysis, polymer **3** can be considered as an oligomer (3–6 monomers).

UV-visible spectra in toluene exhibit a single narrow linear absorption band of 30 nm width, centred at 380 and 376 nm for octupoles **2** and polymer **3**, respectively.

Z-scan measurements were performed in the picosecond range using a sensitive single-shot multi-channel method.[12] With this method, it was possible to perform closed- and open-aperture Z-scans for the same incident pulse to allow simultaneous measurements of the nonlinear refractive index and the nonlinear absorption.[13] Linearly polarised 50 ps TEM_{00} pulses at 1064 nm were delivered by a mode-locked Nd:YAG laser at a repetition rate of 10 Hz. The confocal parameter in our experimental setup was $Z = 23.5$ mm. All compounds were tested in solution (concentration 0.12 mol l^{-1}) in toluene with a 2 mm thick quartz cell. Under our experimental conditions, the nonlinear refraction of the solvent alone was beneath the baseline noise of our apparatus. The nonlinear samples were measured with an incident energy of $E = 37$ μJ and a linear transmittance[14] $S = 0.62$ for n_2 measurements (closed-aperture Z-scan) and $S = 1$ for β measurements (open-aperture Z-scan). The nonlinear refractive indices n_2 and the two-photon absorption coefficients β for all compounds were measured according to the procedure described by Sheik-Bahae *et al.*[14] The experimental data were calibrated using the standard CS_2 reference ($n_{2(CS2)} = 3.5 \times 10^{-18}$ m^2 W^{-1}).

For all three compounds, the measured relative nonlinear index $n_2/n_{2(CS2)}$ was 0.6. None of the octupoles **2** and polymer **3** exhibited detectable two-photon absorption at 1064 nm. This is in accordance with the position of the linear absorption peak wavelengths, giving a two-photon absorption band around 760 nm, far from the exciting wavelength. Hence, octupoles **2** and polymer **3** in solution have an off-resonant nonlinear refractive index close to that of pure CS_2. The expected extrapolated values n_2 for the solutes are close to the best off-resonance nonlinear refractive index data reported for single crystal polydiacetylene toluene-*p*-sulfonate (PTS)[15] ($n_2 = 2.2 \times 10^{-16}$ m^2 W^{-1} @ $\lambda = 1600$ nm). However, one should keep in mind that the extrapolation from solution to the solid state is not straightforward. Nonlinear refraction and absorption measurements on thin solid films of the new polymer **3** are currently being performed so as to investigate this critical issue.



Scheme 2

Stegeman *et al.*[5] defined two figures-of-merit, $W = n_2 I/\alpha\lambda$ and $T = \lambda\beta/n_2$, to assess the suitability of a cubic NLO material for realistic all-optical applications based on the optical Kerr effect. The two criteria, $W >> 1$ or $T << 1$, must be satisfied whether the nonlinearity and the losses in the material are dominated by linear or two-photon absorption, respectively. As no linear (α) or two-photon (β) absorption has been detected in our measurements, we have introduced the limit sensitivities ($\alpha_{min} < 0.05$ m^{-1} and $\beta_{min} < 2 \times 10^{-12}$ m W^{-1}) of our experimental setup. For compounds **2** and **3**, this yields $W > 2200$ and $T < 1$ as an estimation of the lower and upper limits of the figures-of-merit *W* and *T*, respectively. All three materials in solution exhibit very good figures-of-merit. Moreover, the photostability of the polymer in solution has been found to be very satisfactory up to energies per pulse of 120 μJ, *i.e.* intensities up to 18 GW cm^{-2}, corresponding to the damage threshold of the quartz cell.

In conclusion, we have reported the synthesis of the first octupolar polymer and two new octupolar thiophene-based molecules, which exhibit off-resonant third order NLO properties. Due to the absence of detectable linear and nonlinear absorption at 1064 nm, the figures-of-merit are good. Moreover, no modification with respect to the nature of the substituant has been detected on the nonlinear refractive index and on the linear and two-photon absorption properties.

The authors thank Dr A. J. Attias (DMSC, ONERA, France) for his help with the polymer characterisation by SEC.

Notes and references

‡ HRMS analysis of **2a**: $M^{+\cdot} = 837$. **2b**: $M^{+\cdot} = 789$. All NMR data are in agreement with the three proposed structures.

1 D. S. Chemla and J. Zyss, *Nonlinear Optical Properties of Organic Molecules and Crystals*, Academic Press, New York, 1987; H. S. Nalwa and S. Myata, *Nonlinear Optics of Organic Molecules and Polymers*, CRC Press, Boca Raton, 1997.

2 J. Zyss, *Nonlinear Opt.*, 1991, **1**, 3; J. Zyss, *J. Chem. Phys.*, 1993, **98**, 6583; J. Zyss and I. Ledoux, *Chem. Rev.*, 1994, **94**, 77; M. Joffre, D. Yarron, R. Silbey and J. Zyss, *J. Chem. Phys.*, 1992, **97**, 5607; J. Zyss and S. Brasselet, *Opt. Lett.*, 1997, **22**, 1464; S. Brasselet and J. Zyss, *J. Opt. Soc. Am. B*, 1998, **15**, 257.

3 C. Dhenault, I. Ledoux, I. D. W. Samuel, J. Zyss, M. Bourgault and H. LeBozec, *Nature*, 1995, **374**, 339; J. Zyss, S. Brasselet, V. R. Thalladi and G. R. Desiraju, *J. Chem. Phys.*, 1998, **109**, 658; T. Verbiest, K. Clays, C. Samyn, J. Wolff, D. Reinhoudt and A. Persoons, *J. Am. Chem. Soc.*, 1994, **116**, 9320.

4 S. Stadler, R. Dietrich, G. Bourhill and C. Bräuchle, *Opt. Lett.*, 1996, **21**, 251.

5 G. I. Stegeman, in *Nonlinear Optics of Organic Molecules and Polymers*, ed. H. S. Nalwa and S. Myata, CRC Press, Boca Raton, 1997, pp.799–812.

6 D. R. Greve, S. B. Schougaard, T. Geisler, J. C. Petersen and T. Bjornholm, *Adv. Mater.*, 1997, **9**, 1113.

7 A. M. McDonagh, M. G. Humphrey, M. Samoc, B. Luther-Davies, S. Houbrechts, T. Wada, H. Sasabe and A. Persoons, *J. Am. Chem. Soc.*, 1999, **121**, 1405.

8 H. F. Marks, *Encyclopaedia of Polymer Science and Technology*, Wiley, New York, 1964, vol. 1, p. 750.

9 M. G. Hill, J. F. Penneau, B. Zinger, K. R. Mann and L. L. Miller, *Chem. Mater.*, 1992, **4**, 1106.

10 F. Chérioux, L. Guyard and P. Audebert, *Chem. Commun.*, 1998, 2225.

11 F. Chérioux, P. Audebert and P. Hapiot, *Chem. Mater.*, 1998, **10**, 1984.

12 A. Marcano, O. H. Maillotte, D. Gindre and D. Métin, *Opt. Lett.*,1996, **21**, 101; F. E. Hernandez, A. Marcano and O. H. Maillotte, *Opt. Commun.*, 1997, **134**, 529.

13 F. Chérioux, P. Audebert, H. Maillotte, L. Grossard, F. E. Hernandez and A. Lacourt, *Chem. Mater.*, 1997, **9**, 2921.

14 M. Sheik-Bahae, A. A. Said, T. Wei, D. J. Hagan and E. W. Van Stryland, *IEEE J. Quantum Electron.*, 1990, **26**, 760.

15 B. W. Lawrence, M. Cha, J. U. Kang, W. Torruellas, G. Stegeman, G. Baker, J. Meth and S. Etemad, *Electron. Lett.*, 1994, **30**, 5.

Communication 9/05899K