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Nonlinear optical properties of open-shell polychlorotriphenylmethyl radicals

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Abstract

The second-order nonlinear optical (SONLO) response of a series of the highly chemically and thermally stable polychlorotriphenylmethyl monoradicals **1**–**8** has been studied by Hyper-Rayleigh Scattering. These radicals exhibit relatively high nonlinear optical (NLO) responses with β values ranging from 118×10^{-30} to 755×10^{-30} esu, which may result from an enhancement of the SONLO activities according to their open-shell electronic state. Hyperpolarizability data for radicals **1**–**8** have also been correlated with their redox potentials, correlation that has turned out to be linearly proportional either with the oxidation or the reduction potentials. These data have been justified in terms of molecular orbital energies. Finally we have successfully explored the capacity of radicals **1**–**8** to participate in a molecular switching array involving two main steps, an acid/base reaction and a redox process. The presence of open-shell character for this family of compounds makes them attractive candidates to design new multifunctional materials that would simultaneously possess magnetism and NLO.

Keywords: Radical; Second-order; NLO; HRS; Electrochemistry

1. Introduction

In the last few years, the interest to develop novel second-order nonlinear optical (SONLO) materials has considerably increased due to their potential application in emerging optoelectronic technologies [1]. A major advantage of the use of photonics instead of electronics is the possibility to increase the speed of information processes such as photonic switching and optical computing. Traditionally, materials exhibiting SONLO behavior were inorganic crystals, such as lithium niobate ($LiNbO_3$) and potassium dihydrogenphosphate (KDP) [2]. However, organic materials, such as organic crystals and polymers, have been shown to offer better nonlinear optical (NLO) and physical properties, such as ultrafast response times, lower dielectric constants, better processability and a remarkable resistance to optical damage, when compared to inorganic materials. Moreover, the ease of modification of organic molecular structures makes it possible to synthesize tailor-made molecules whose properties may be fine-tuned at will. Most of the efforts to discover new molecular chromophores having large SONLO properties have been focused on closed-shell organic species. However, more recently, a large interest has been devoted to the investigation and development of NLO materials having open-shell electronic structures [3]. As it has been recently pointed out, species having open-shell electronic states can exhibit very large first-order hyperpolarizability (β) in comparison with analogous closed-shell systems, thanks to the presence of accessible low-lying charge transfer electronic states. In spite of this interest, only a few examples of organic open-shell species showing second-order hyperpolarizabilities have been up to now described, mostly

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due to the high instability of these species [4]. For instance, the NLO response in solid state of a family of α-nitronyl nitroxide radicals (NIT) was measured by the Kurtz-Powder technique due to their low stability in solution [5]. The *p*-nitrophenyl substituted radical (NPNN) turned out to be more stable in solution making possible to measure its NLO response with the EFISGH technique, yielding a β value of 6.24×10^{-30} esu [6].

In our group, we focused our attention in the development of new NLO materials using polychlorinated triphenylmethyl (PTM) radical units as building blocks. The interest for these radicals is threefold: (1) PTM radicals have their open-shell centers sterically shielded by six bulky chlorine atoms in order to increase their life expectancies and thermal and chemical stabilities [7], (2) PTM radicals exhibit a $Ar^1Ar^2Ar^3Z$ geometry with a propeller-like conformation (see Fig. 1) characteristic of NLO octupolar systems [8], fact that aim us to expect second-order NLO responses and (3) their magnetic character opens new possibilities to the design of new multifunctional materials that would simultaneously possess magnetism and NLO properties [9].

In this paper, the capability of PTM monoradicals to generate NLO responses as octupolar materials has been analyzed and their corresponding hyperpolarizability values measured using the Hyper-Rayleigh Scattering (HRS) technique [10].

2. Experimental

Reagents were obtained commercially and used as purchased. The series of radicals **1**–**8** was prepared as previously described [11]. Molecular nonlinear coefficients were obtained in dichloromethane solution using the harmonic light scattering experiment. The quadratic hyperpolarizability (β) was derived from the intensity of the incoherent scattered light at 532 nm. The Q-switched Nd^{3+}:YAG laser operating at 1064 nm yields a pulse of 10 ns duration at 10 Hz repetition rate. The incident pulse intensity is changed by a set composed of a computer controlled rotating half-wave plate followed by a Glan-Taylor polarizer. The fundamental laser beam was focused on the center of the 2 cm path quartz cell with a long focal length plano-convex lens ($f = 150$ mm). The light scattered perpendicular to the incident beam was detected with a photomultiplier tube (PMT). A low-pass filter was used to filter out Rayleigh scattered infrared light. An interference filter (532 nm central wavelength and 3 nm transmission bandwidth) permitted a second harmonic detection. The electrical signal from the PMT is first amplified then digitized by a lab-made box-car. The accuracy of our set-up on the determination of β was checked on a *p*-nitroaniline sample in methanol. The error is estimated to be approximately ±15%. Absorption and fluorescence were recorded on a Cary 5E spectrophotometer and Edinburgh Instruments spectrometer, respectively. Note that Absorption at 532 nm is small and almost similar for all the investigated compounds. Therefore the resonant enhancement of β at the harmonic laser frequency is expected to be similarly weak and cannot account for the experimental tendency. Fluorescence spectra were collected with spectroscopic solvents quality. The standard for the fluorescence quantum yield determinations with solvent refractive index correction was quinine bisulfate in 1 N H_2SO_4 ($\phi_f = 0.55$) and the experimental errors are ±10%. All compounds have been investigated at 532 nm. Weak emissions have been recorded for **1** ($\phi_f = 0.09$), **2** ($\phi_f = 2 \times 10^{-3}$), **5** ($\phi_f = 0.19$), **6** ($\phi_f = 3 \times 10^{-3}$) and **8** ($\phi_f = 0.04$). Nevertheless, no direct correlation between emission and measured β values has been noticed. Electrochemical experiments were performed with an Electromat 2000 system (ISMP Technologies), using a platinum wire as working electrode and a Ag/AgCl as reference electrode. Anhydrous CH_2Cl_2 was freshly distilled over P_2O_5 under nitrogen. Commercial tetrabutylammonium hexafluorophosphate (Fluka, electrochemical grade) was used as the supporting electrolyte.

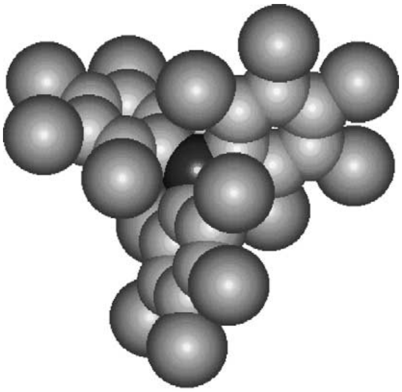
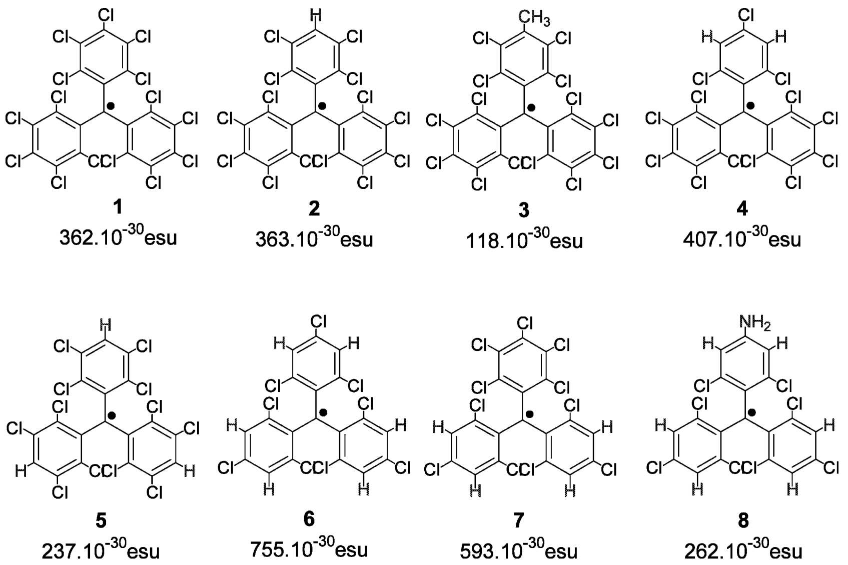


Fig. 1. Molecular conformation of radical **1** showing the octupolar geometry (D_3 symmetry) adopted by this radical.

3. Results and discussion

3.1. HRS experiments

The NLO octupolar response of PTM radicals **1**–**8** was obtained from HRS experiments using dichloromethane as solvent. Data reported in Scheme 1 show that radicals **1**–**8** exhibit relatively high NLO responses, with β values ranging from 118×10^{-30} to 755×10^{-30} esu. This fact is not surprising since, as previously mentioned, this family of radicals is structurally very similar to the octupolar symmetry of crystal violet,



Scheme 1. Series of PTM radicals **1**–**8** and its corresponding hyperpolarizability β values.

which exhibits a large β value. In fact, both types of compounds have the general formula $Ar^1Ar^2Ar^3Z$, where Ar^i denotes a substituted aromatic group and Z is an sp^2 hybridized atom (a cationic C^+ center in crystal violet and an open-shell $C^\bullet$ center in triphenylmethyl radicals). Nevertheless, it is important to emphasize that in spite of exhibiting similar $Ar^1Ar^2Ar^3Z$ topologies, the β values obtained for PTM radicals may be up to five times larger than the one reported for the related closed-shell crystal violet compound (150×10^{-30} esu).

These results point out to an enhancement of the second-order NLO (SONLO) activities of radicals **1**–**8** according to their open-shell electronic character, which is expected to enhance β values with respect to their closed-shell counterparts due to the presence of accessible low-lying charge transfer electronic states. However, before extracting any conclusion, it is convenient to revise the nature of PTM radicals. Indeed, a closer look to this family of radicals reveals than in addition to their $Ar^1Ar^2Ar^3Z$ topology and their open-shell character, they are composed of three individual building blocks (three substituted phenyl groups), each one having a SONLO contribution by themselves. More precisely, 1,3,5-trichlorobenzene (TCB) and pentachlorobenzene (PCB) have an octupolar component and belong, respectively, to D_{3h} (pure octupolar system) and C_{2v} (with dipolar and octupolar contributions) group of symmetry. The experimental β values found for PCB and TCB were 8×10^{-30} and 22×10^{-30} esu, respectively. If a synergistic effect takes place, this will greatly contribute to enhance the SONLO responses of this type of radicals. Along this line, the comparison between purely octupolar radical compounds **1** and **6** may result very interesting. Both systems exhibit a D_3 symmetry and are composed of three individual building blocks with SONLO contributions based on PCB and TCB, respectively. HRS measurements show that the β value of **1** (362×10^{-30} esu) is lower than that obtained for **6** (755×10^{-30} esu). Interestingly, such values follow the tendency found for the molecular hyperpolarizabilities derived from each individual octupolar block, suggesting that a synergetic effect between individual building blocks may occur. Nevertheless, the absorption of PCB and TCB are so different from related radicals **1** and **6** that any significant conclusion about the 'super-octupolar' nature of the PTM radicals remains uncertain.

3.2. Electrochemical experiments

To give more insight into the electronic configuration of PTM radicals shown in Scheme 1 and its potential influence on the SONLO response, electrochemical experiments were carried out. Cyclic voltammetry studies were done in CH_2Cl_2, with $n\mathrm{Bu_4NPF_6}$ (0.1 M) as supporting electrolyte (vs. Ag/AgCl) and using a Pt wire as a working electrode. The cyclic voltammetry response of radicals **1**–**8** show in all the cases two different reversible redox processes that correspond to an oxidation and a reduction process. Both reversible processes arise from oxidation of the radical to the cationic species whereas the reversible reduction process is associated to the reduction of the triphenylmethyl radical unit to its corresponding anionic form (see Fig. 2).

Interestingly, the representation of the hyperpolarizability β value in front of the reduction or oxidation redox potentials of radicals **1**–**8** yields a linear dependence (see Fig. 3). Indeed, as the oxidation potential

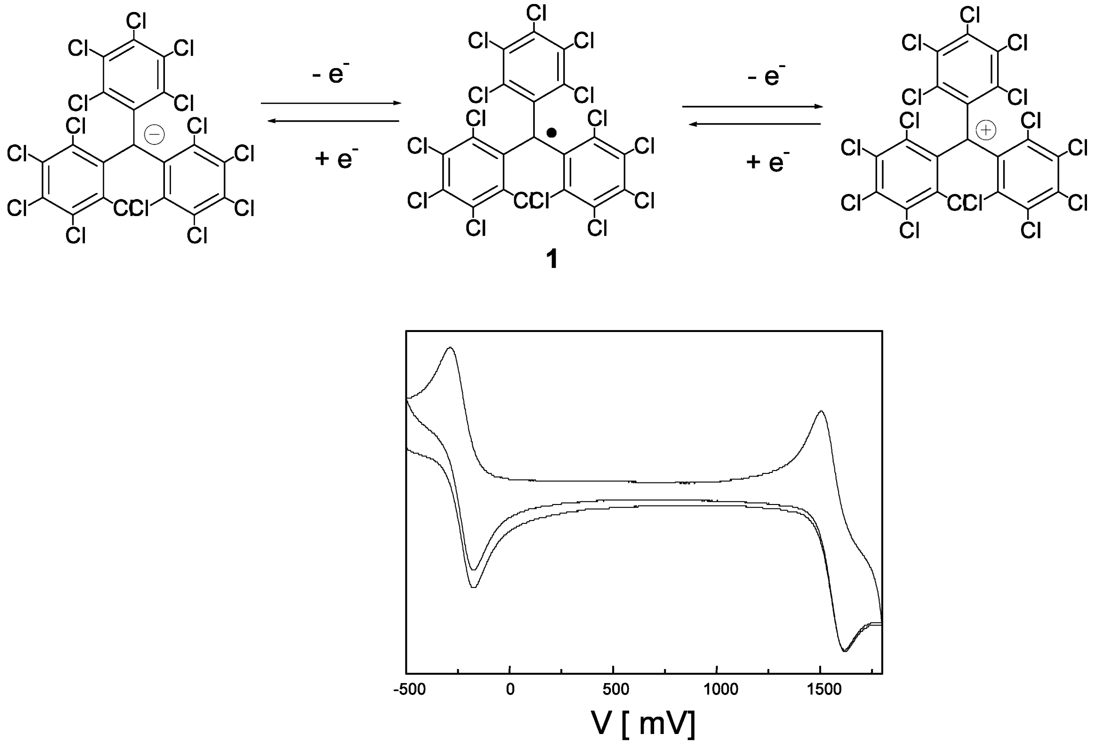


Fig. 2. The cyclic voltammetry of radical **1** exhibits two clear redox processes corresponding to the oxidation of the radical species to the cation and reduction of the radical to its corresponding anionic form.

decreases, the hyperpolarizability β value increases whereas on the contrary, the easier to reduce the lower results β. As an example, the representation of the oxidation potential in front of the β value for radicals **1**–**8** is shown in Fig. 3.

This is an indication that the orbital involved in the redox phenomena, most likely the SOMO orbital, is the same either in the oxidation or in the reduction process, confirming the existence of a direct correlation between the energy of the electronic transition and the SONLO response.

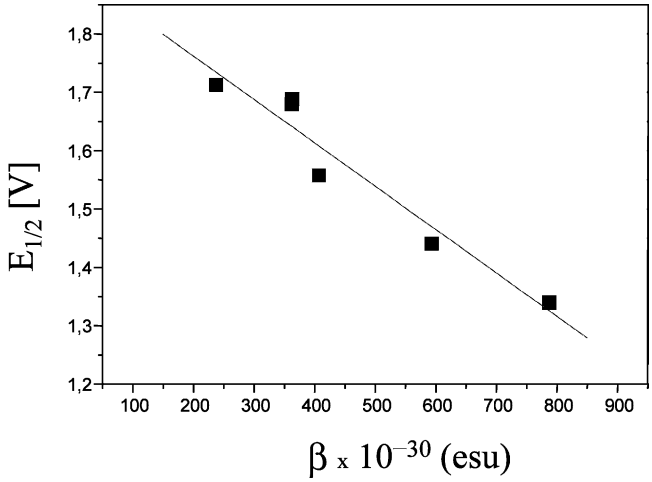


Fig. 3. Representation of the oxidation potential of the series of radicals **1**–**8** in front of their hyperpolarizability β values. Solid squares represent the experimental values whereas the line represents the best linear fit.

3.3. Switching properties

The field of molecular switches has attracted great interest in the last few years because of their relevance in the development of molecular electronics and photonics [12,13]. Several examples of supramolecular devices whose optical properties (i.e. photochromism [14], luminescence and/or optical nonlinearity) can be switched (or modulated) by different external stimuli have been reported [15]. Due to this interest we have explored the molecular switching array shown in Fig. 4, which involves two main steps: (1) the reversible reduction of radical **1** to its corresponding anionic form and (2) subsequent reversible protonation to give the corresponding precursor hydrocarbon. The objective is to control or tune the open-shell character and/or NLO response of radical **1**, as a representative example of the radical series shown in Fig. 1.

3.3.1. Redox process

The study of the scan rate (υ) dependence of the two reduction redox process observed for **1** showed a linear dependence of the peak current with respect $\upsilon^{1/2}$ suggesting that this electrochemical process is reversible and diffusion-controlled. Potential-controlled electrolysis experiments of **1** were also carried out confirming the

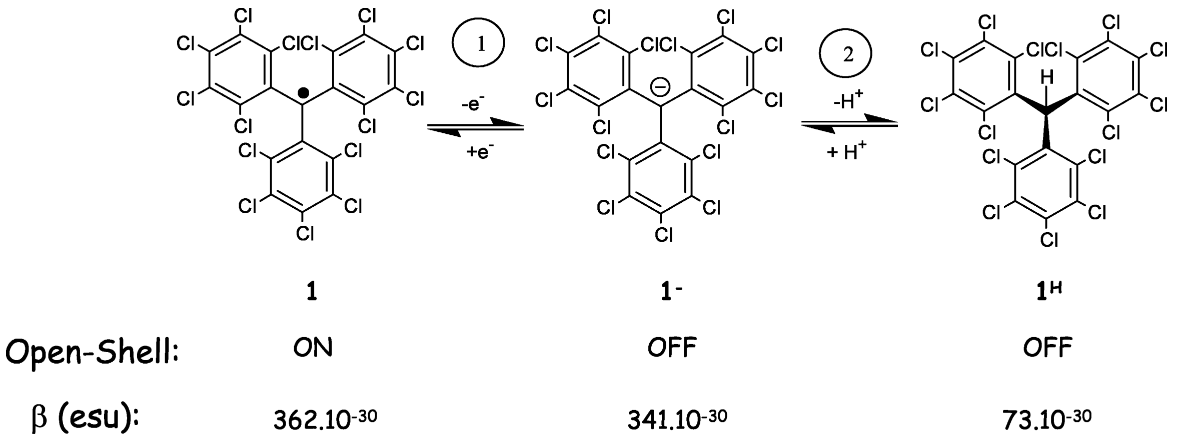


Fig. 4. A three steps molecular switching array established for radical **1** that involves two main external stimuli: a redox reaction that interconverts the radical to its corresponding anionic form and an acid/base reaction that converts the anionic form into its protonated form. The corresponding hyperpolarizability β values and the open-shell character of each one of the species involved in the molecular switching array is also shown. The β value for the anionic form $\mathbf{1}^-$ is overestimated due to the strong interference of an absorption at 532 nm.

possibility to reduce reversibly the target molecule. As an example, the reversible interconversion example between radical $\mathbf{1}^\bullet$ and its corresponding anion $\mathbf{1}^-$ is shown in Fig. 5. This fact is an indication of no structural changes or decomposition in the time scale of the experiment and that the corresponding ionic species can be generated, fact that confirms the validity of using redox properties as the first switching capacity. However, in spite of the feasibility of such redox induced interconversion, it did not resulted effective for the establishment of a NLO switch. Indeed, even though the SONLO response for $\mathbf{1}^-$ was measured to be 341×10^{-30} esu, such value is not reliable since the anionic species exhibit a strong absorption at 532 nm ($\varepsilon \sim 25\,000$), which is expected to strongly interfere with the SONLO response, therefore leading to overestimated values.

3.3.2. Acid–base reaction

This step consists in the protonation and deprotonation of the anionic form $\mathbf{1}^-$ for which pK_a-modulation is possible. The NLO response decreases as the pH of the solution increases, being under acidic condition when the protonated species is generated. SONLO response of the hydrocarbon precursor of **1** with three arylic groups covalently connected with a tetrahedral geometry around an sp^3 carbon atom was studied. Experimental HRS measurements show that its macroscopic molecular hyperpolarizability was $\beta = 73 \times 10^{-30}$ esu, which is considerably lower than the one obtained for its related

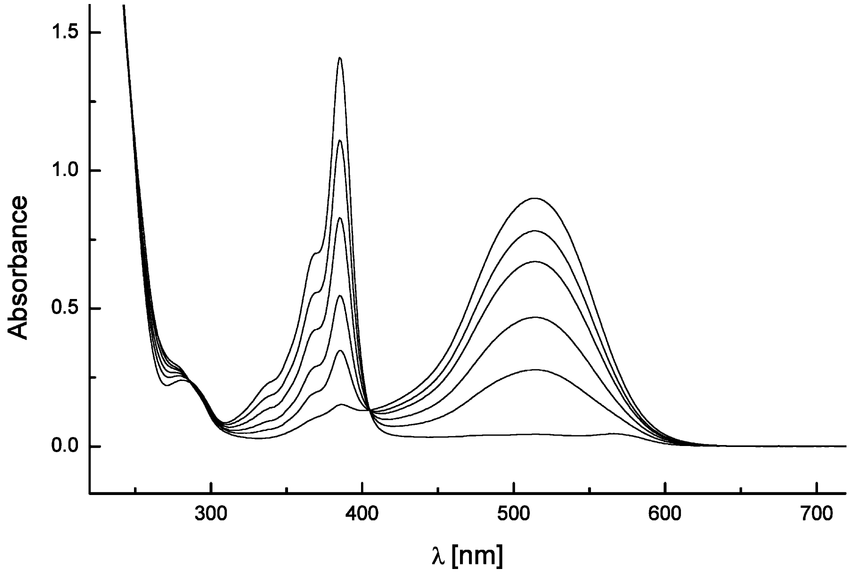


Fig. 5. Evolution of the UV–Vis (top) during the course of the reduction of radical **1**. The interconversion has been shown to be fully reversible along different cycles.

octupolar open-shell radical $1^{\bullet}$ (360×10^{-30} esu). Such a variation may come from: (i) variation of the structure from a C_3 symmetry to a D_3 one, exhibited by radical **1**, (ii) an enhancement of the SONLO response due to the open-shell character of radical **1**, or (iii) a mixture of both.

4. Conclusion

In summary, the series of PTM radicals **1**–**8** have been shown to exhibit relatively large SONLO responses according to their octupolar character. Moreover, hyperpolarizability data for radicals **1**–**8** have also been correlated with their redox potentials, correlation that has turned out to be linearly proportional either with the oxidation or the reduction potentials. The results presented in this work open new possibilities to the design of new multifunctional materials and/or switchable molecular materials that would simultaneously possess magnetism and NLO properties.

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