Enhanced nonlinearities of functionalized single wall carbon nanotubes with diethynylsilane derivatives

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1. Introduction

Carbon nanotubes (CNTs) exhibit very interesting magnetic, electronic and transport properties that are required for the manufacture of molecular devices [1–3]. Furthermore, these carbon-based materials also exhibit unique mechanical and structural properties having attracted the attention of multidisciplinary research groups. A survey of works has been reported in the literature showing various applications as biosensors [4,5], photovoltaics devices [6], field effect transistors [7,8], solar cells [9,10], encapsulating of different materials [11,12], adsorbents of inorganic and organic compounds [13,14], catalysis [15], among others. The unique properties of this class of carbon-based material open a large perspective of applications in different areas, in special in the nanotechnology and health fields. Hence, CNTs have been investigating by experimental and theoretical groups giving emphasis in structural and electronic modifications resulting from the decoration of the CNT surface [16–18]. A better processing of the single wall carbon nanotube (SWCN) is found when the supramolecular complexes are formed, since they are insoluble in usual solvents. In addition, some practical applications of SWCN have been explored due to the cylindrical geometry and their nanometric scale. Besides, some materials with high resistance are required for applications in nanoelectronics [19,20]. Thus, the composites of CNTs are prominent candidates due to the synergistic effect observed for the nonlinear optical and electric properties [19,20]. Therefore, these materials can be envisioned for the manufacture of nonlinear optics (NLO) devices.

CNTs having well-defined atomic structure, with high length to diameter ratio, associated with their chemical stability constitute a one-dimensional molecule [1–3]. Few experimental and theoretical papers have been reported on SWCN derivatives with potential applications in the field of nonlinear optics [17,18,21–25]. Single- and multi-walled carbon nanotubes are characterized as a nonlinear material having large second hyperpolarizability (β) [21–23,25]. Theoretical studies using a point–dipole interaction model demonstrated that the nanotubes display large γ values compared to the fullerene having the same number of carbon atoms [26]. Furthermore, it was observed that the increasing of the diameter of armchair and zigzag CNT contributes for the enlargement of the values of this nonlinear coefficient. Early theoretical studies show an empirical exponential law of the static γ for armchair and zigzag nanotubes with topological dimensions [25]. De Dominicis et al. [23] performed experimental investigation of the second-harmonic generation (SHG) of SWCN films at nanosecond time scale, which was observed only in the nanotubes synthesized in laboratory in contrast with the commercially available, indicating a certain degree of anisotropy of prepared samples. Previous experimental work demonstrated the third-order nonlinearities of SWCN by the THG experiment at the femtosecond time scale [21]. Furthermore, for chiral nanotubes it was observed that the quadratic susceptibility became smaller as the nanotube diameter is increased, while this nonlinear response is not observed for the armchair and zig-zag nanotubes [24].
Theoretical investigation has used the strategy of attaching some substituted stilbenes with donor (D) or acceptor (A) groups on the external surface of the armchair (5,5) SWCN to increase the first hyperpolarizability ($\beta$) via covalent bond [17]. The CNTs have a null value of $\beta$ due to their highly symmetric structure. The $\beta$ value for the chemically modified nanotube enhanced up to 70% relative to the free 4,4'-substituted stilbene according with the DFT calculations [17]. Moreover, it was observed that $\beta$ values for substituted derivatives are increased almost linearly with the strength of the electron D or A groups as indicated by the Hammett parameter. In addition, SWCN nanotubes with Zn(II) porphyrin adsorbed showed nonlinear properties according with recent DFT studies [18]. In Ref. [18] De Souza et al. claimed that the breaking of symmetry due to the interaction with Zn(II) porphyrin adsorbed on CNT is the major reason for the remarkable increase of the $\beta$ value for the hybrid nanocomposite.

Having in mind the promising extremely applications as for fabrication of devices for use in nanotechnologies, molecular models of chemically modified SWCN were proposed in this work to obtain derivatives with enhanced values of the $\beta$ hyperpolarizability. Materials with large values of this nonlinear coefficient are required for applications as electro-optical modulation and all-optical switching, among others [27]. For donor–acceptor alicyclic organic molecules the magnitude of $\beta$ is strongly correlated with the molecular asymmetry, the donor–acceptor pair strength, the size of conjugation between the D and A substituents as well as their nature and the molecular conformation [27–31]. Furthermore, the lowest energy electronic absorption (charge transfer process) contributes to enhance the first hyperpolarizability according to approaches based on the perturbation theory [27]. Also, the transparency and stability are fundamental for nonlinear materials candidates for use in opto-electronic and photon [27]. When a substitution is performed on the SWCN surface the result is a modification of their optical and electrical properties, similar to those observed when inclusion defects are verified [2, 17, 18, 32, 33]. Therefore, in this work we made use of donor or acceptor substituents that would contribute to increase charge transfer between the armchair CNT, which is a metallic nanotube, and the diethynylsilane (PDES) oligomers, and so, to the enhancement of the $\beta$ magnitude for this carbon-based material.

In the present Letter it was performed a molecular modeling of the CNT derivatives with enhanced nonlinear responses, using DFT calculations with the B3LYP functional employing the 6-31G(d) basis set. The goal of the present work was to assess the functionalized SWCN with PDES decamers that are candidates' nanocomposites as second-order nonlinear materials of high performance. The introduction of Si atoms on nanotubes and fullerene structures has been investigated since it can be very useful as a site to functionalization of these carbon-based materials as well as to increase the material resistance [19, 20, 32, 33]. Furthermore, the Si atom incorporated into nonlinear materials is interesting due to applications in nanoelectronics. The literature reports that the covalent reaction of SWCN with polymers have been performed by experimental groups resulting in a marked increase of the solubility of the tubes in a range of solvents even at low degree of functionalization [2, 19, 20]. Therefore, it can be expected that the derivatives investigated in the present work will display a better processing facility in comparison with the nanotube itself, which is useful for the manufacture of devices, as well as to open a novel chemistry branch for this important class of nonlinear materials.

2. Methodology

Quantum chemical methods have been considered as a useful approach for the prediction of the hyperpolarizabilities of small and large molecules, as well molecular clusters [17, 18, 27–31, 34, 35]. In particular, the DFT methods have been satisfactorily applied to large molecules for which more rigorous methods such as Muller–Plesset perturbation theory (MP) and coupled cluster (CC), that estimate the first hyperpolarizability ($\beta$) magnitude with increased accuracy, are prohibitive [27, 34, 35]. Therefore, DFT methods are the best choice in terms of accuracy and computational time. The choice of the basis set also plays a role in the quality of the results [27, 34, 35]. According to the literature, calculations using a large basis set with polarization and diffuse functions are required to reproduce the experimental magnitude of $\beta$ [27, 34, 35]. Nonetheless, several systematic theoretical studies indicate that the inclusion of an augmented set does not promote large differences in the $\beta$ values for extended systems, with results found in accordance with the experimental data even when medium-size basis sets are used [17, 18, 27, 34, 35]. Therefore, for very large molecules such those studied in the present work, the 6-31G(d) basis set was selected for structural determination as well as for the calculation of $\beta$ values. It is opportune to mention that DFT calculations of the static $\beta$ were recently performed for PDES decamers substituted with electron donor and acceptor groups [36]. Very enhanced $\beta$ values were obtained for all di-substituted oligomers when compared to the oligomer missing the D–A pair using both the pure and hybrid DFT methods. The results strongly suggested that di-substituted PDES decamers are potential building blocks for molecular-based materials with second-order nonlinear responses, what strongly motivated the present work on CNT composites.

Firstly a PDES decamer was linked on the external surface of the armchair (5,5) CNT with 14 Å length and 6.8 Å diameter, both in transversal (Figure 1, structure Nano-1a) and longitudinal (Figure 2, structure Nano-1b) orientations. Then, electron-donor and/or acceptor groups were attached to its ends (structures Nano-IIa and Nano-IIb, Figure 1 and structures Nano-Ilb and Nano-IIblb, Figure 2). When donor–acceptor pair is present (Nano-IIa and Nano-IIb, Figure 1), two possibilities were explored to increase the molecular asymmetry. In the first case, the linking is performed near to the donor group, whereas in the second one the CNT bonding is near to the electron-acceptor group. Therefore, the D–A oligomer is transversal to the tubular structure of the SWCN. Besides of accounting for the effect of the D–A pair, we also performed calculations on the structure where the D–A pair is missing in the oligomer structure (structures Nano-la and Nano-IIa).

The geometries of the CNT derivatives and non-substituted and substituted PDES decamers were fully optimized using DFT method with the B3LYP hybrid functional [37, 38] and the 6-31G(d) polarized basis set [39] (hereafter abbreviated as B3LYP/6-31G(d)). DFT calculations of first hyperpolarizability ($\beta$) and polarizability ($\alpha$) were performed with the same method used for geometry optimizations, namely B3LYP/6-31G(d). It must bear in mind that all hybrid functional overestimates the first hyperpolarizability [34, 40, 41], with the sensitive of the method being dependent on the magnitude of the property. For instance, for p-nitroaniline (p-NA) the B3LYP/6-31G(d) is only 24% higher than the experimental value, however, for molecules with $\beta > 500 \times 10^{-30}$ cm$^2$ esu$^{-1}$ the difference can be larger than 100% (unpublished results). The basis set also play a role as pointed out by Suponitsky et al. [34], who recommend the 6-31+G(d) basis set for large molecules. For p-NA, commonly used as probe molecule, the B3LYP/6-31G(d) and B3LYP/6-311G(d) levels show essentially the same $\beta$ value, equal to $11.5 \times 10^{-30}$ cm$^2$ esu$^{-1}$ (unpublished data), which is around 20% larger than the reference data. It is also opportune to make clear that we are looking for trends over a series of analog molecules and not necessarily analyzing absolute values of electrical properties, thus it is expected a smaller error on the relative values.

The NLO properties were calculated using the coupled perturbed Kohn–Sham (CPKS) approach. The CPKS method is based on the
finite field (FF) method [42], where the tensor elements $\beta_{ijk}$ (where $i$, $j$ and $k$ are equal to $x$, $y$ and $z$, respectively) are obtained by partial derivatives of the molecular energy perturbed by the external time-dependent electric field. From the tensor elements $\beta_{ijk}$, the Cartesian components $\beta_x$, $\beta_y$, and $\beta_z$ can be calculated according to Eq. (1) [43]:

$$\beta_i = \frac{1}{3} \sum_{i}^{} (\beta_{iik} + \beta_{ikk} + \beta_{kik}) \quad \forall \ k = x, y, z; \ i = x, y, z$$

(1)

Thus, the total molecular first hyperpolarizability ($\beta_{mol}$) is calculated according to Eq. (2):

$$\beta_{mol} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}$$

(2)

The GAUSSIAN quantum mechanical package [44] uses the relationship $\beta_{ij} = \beta_{ji}$ and provides a tensor with 10 elements only. The averaged polarizability is evaluated according to Eq. (3) [43]:

$$\alpha_{av} = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

(3)

All calculations were carried out using the GAUSSIAN-03/09 program [44].

3. Results and discussions

The B3LYP/6-31G(d) fully optimized geometries for the model systems studied here are depicted in Figures 1 and 2 and the
electrical properties for isolated nanotube and oligomers, and the nonocomposites, are given in Table 1. The CNT derivative with the PDES decamer having the dicyanovinyl (A) and propyl (D) groups that is linked transversely to one nanotube, structure Nano-IIa (Figure 1b), presents the largest value of $\mu_{mol}$ at the DFT level, in spite of being smaller than the corresponding value for the isolated di-substituted oligomer (Oligom-IIa, Table 1). The vector component of $\mu$ along the dipole moment direction (denominated $\mu_{vec}$ [43]) is also quoted in the footnote of Table 1 for the nanocomposite Nano-IIa and respective free oligomer, which is the quantity measured in the electric field-induced second-harmonic generation (EFISH) experiment. The deviation between $\mu_{vec}$ and $\mu_{mol}$ can be considered small, so the second-order response to the applied field will be sampled in EFISH measurements. Furthermore, very large values of $\mu_{mol}$ ($>2000 \times 10^{-30} \text{ cm}^2 \text{ esu}^{-1}$) were also obtained for all CNT derivatives designed, with the values for structures Nano-IIb, -IIla and -IIlb being slightly bigger than the respective values for the corresponding free oligomers. Despite the error on the methodology that overestimates the absolute $\mu$ values, these are still quite large when compared to reference systems in the literature. For instance, the bacteriorhodopsin (bR), one of the three photosensitive system of nature, possesses very large molecular $\mu$, around $2100 \times 10^{-30} \text{ cm}^2 \text{ esu}^{-1}$ measured at 1064 nm using hyper-Rayleigh scattering technique [45]. An analysis of Table 1 reveals that the oligomer-CNT composites exhibit $\mu$ values close to the corresponding free oligomers and so, a composite with very high value of $\mu$ can be designed by choosing an adequate oligomer having very large value of $\mu$. In addition to, the CNT derivatives show smaller values of the HOMO–LUMO energy gap in comparison with the isolated substituted oligomers. These results indicate the potential use of these derivatives as nanoelectronics devices due to the very small band gap. It is worth saying that calculated B3LYP band gap is in good agreement with experimental measures [46]. Moreover, recent theoretical work showed that the B3LYP/6-31G(d) method calculates the band gap of metallic CNTs in excellent agreement with the experimental values [47]. Furthermore, according to the simple approach of two electronic levels for molecules that display electron transfer, the $\mu$

![Figure 2. B3LYP/6-31G(d) fully optimized structures for the Nano-Ib (a), IIb (b) and IIIb (c) nano-derivatives.](image)

**Table 1**

B3LYP/6-31G(d) calculated electric properties$^a$ for the nanocomposites Nano-Ia, Ib, IIa, IIb, IIIa and IIIb and the corresponding isolated nanotube and substituted oligomers (See Figures 1 and 2).

<table>
<thead>
<tr>
<th>Nanocomposites</th>
<th>Nano-Ia</th>
<th>Nano-Ib</th>
<th>Nano-IIla</th>
<th>Nano-IIb</th>
<th>Nano-IIIa</th>
<th>Nano-IIIb</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_{uv}^a/\text{eV}$</td>
<td>0.78</td>
<td>0.77</td>
<td>0.59</td>
<td>0.77</td>
<td>0.78</td>
<td>0.77</td>
</tr>
<tr>
<td>$\mu/\text{Debye}$</td>
<td>10.07</td>
<td>13.17</td>
<td>5.74</td>
<td>27.62</td>
<td>33.71</td>
<td>10.32</td>
</tr>
<tr>
<td>$\lambda/10^{-25} \text{ cm}^3$</td>
<td>5426</td>
<td>5994</td>
<td>6597</td>
<td>6212</td>
<td>6499</td>
<td>6551</td>
</tr>
<tr>
<td>$\mu_{mol}/10^{-30} \text{ cm}^2 \text{ esu}^{-1}$</td>
<td>1799</td>
<td>1820</td>
<td>21991</td>
<td>2390</td>
<td>7628</td>
<td>7509</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Isolated Nanotube and Substituted Oligomers</th>
<th>Free Nanotube</th>
<th>Oligom-I</th>
<th>Oligom-IIla</th>
<th>Oligom-IIb</th>
<th>Oligom-IIIa</th>
<th>Oligom-IIIb</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_{uv}^a/\text{eV}$</td>
<td>0.79</td>
<td>1.76</td>
<td>1.15</td>
<td>1.84</td>
<td>1.69</td>
<td>1.59</td>
</tr>
<tr>
<td>$\mu/\text{Debye}$</td>
<td>0.0</td>
<td>10.87</td>
<td>4.96</td>
<td>27.36</td>
<td>33.97</td>
<td>7.26</td>
</tr>
<tr>
<td>$\lambda/10^{-25} \text{ cm}^3$</td>
<td>2189</td>
<td>3261</td>
<td>4876</td>
<td>3544</td>
<td>4216</td>
<td>3812</td>
</tr>
<tr>
<td>$\mu_{mol}/10^{-30} \text{ cm}^2 \text{ esu}^{-1}$</td>
<td>1.15</td>
<td>2553</td>
<td>33170</td>
<td>2266</td>
<td>7592</td>
<td>7487</td>
</tr>
</tbody>
</table>

Polarizability: ($a$) 1 a.u. = $1.48184709 \times 10^{-25} \text{ cm}^3$; first-hyperpolarizability ($b$): 1 a.u. = $8.639418 \times 10^{-15} \text{ cm}^3 \text{ esu}^{-1}$.

$^a$ Dipole moment: 1 a.u. (Bohr-electron) = $2.541765 \text{ Debye} = 2.541765 \times 10^{-18} \text{ esu-cm}$.

$^b$ $\epsilon_{uv}$: energy gap (HOMO–LUMO difference). 1 a.u. = $27.2114 \text{ eV}$.

$^c$ The $\mu_{vec}$ (the vector component of $\mu$ along the dipole moment direction [43]) values for Nano-IIla and respective free oligomer structure are $-18118$ and $-32669 \times 10^{-30} \text{ cm}^2 \text{ esu}^{-1}$ respectively.
values are directly related to the oscillator strength and inversely to the energy gap [27]. Therefore, one direction to optimize the investigated systems is increasing the force of oscillator and so, the chromophores substituent selection is crucial to set up the photophysical properties that will contribute for optimized nonlinear response.

The results reported in Table 1 indicate that the introduction of the donor–acceptor decamer transversely or longitudinally to the nanotube external surface is an efficient strategy to enhance the nonlinear response, even though the predicted $\beta$ values can be smaller than the corresponding free polymer (see Table 1). Moreover, the strength of the $D$–$A$ pair, as well as the site selected for the linking of the PDES decamer to the nanotube external surface is fundamental to enhance the value of the $\beta_{\text{mol}}$ as can be observed by comparing, for example, the results for the Nano-IIa and Nano-IIIa derivatives, which have quite different $\beta$ magnitudes. The Nano-Ia nanocomposite, where the $D/A$ pair is missing, having the oligomer introduced transversely to the nanotube surface, has $\beta_{\text{mol}}$ magnitude with similar magnitude to the corresponding Nano-Ib species that has the oligomer linked longitudinally and also misses the $D$ or $A$ groups. These results demonstrated the fundamental role of the $D/A$ pair to polarize the CNT in order to enhance the nonlinear coefficients.

The Nano-IIa derivative with the oligomer having a dicyanovinyl-propyl acceptor–donor pair that is transversal to the nanotube external surface has a $\beta$ magnitude slightly lower than that predicted for the free polymer (≈34% lower). This might be due to the position of substitution, with the tube linked in the middle of the chain, decreasing the effective conjugation length compared to the free polymer. For the structure Nano-IIa, the value drops to $7628 \times 10^{-30}$ cm$^2$ esu$^{-1}$, which is due to the very short chain between the push–pull moieties, namely the phenylamine and the CNT. Therefore, a very simple empirical structure–property relationship might be proposed saying that the insertion of the tube on a push–pull polymer decreases the non-linear response and, this effect is much more pronounced as the bond position approaches to the electron-donor group, which is an evidence of the electron-withdrawing characteristic of the CNTs. The Nano-IIa derivative presents the highest value of $\beta$ among the hybrid systems investigated as well the smallest HOMO–LUMO energy gap. Therefore, the introduction of a PDES $\pi$-conjugated oligomer, having $D/A$ groups, on the CNT surface promotes markedly increase on the polarization of these systems. Thus, it can be concluded that a charge transfer process between the CNT and the PDES oligomers should take place. Recent resonance Raman spectroscopic studies demonstrated that such process occurs between the CNTs and the polyaniline $\pi$-conjugated polymer nanocomposites [19,20].

The linking of the oligomers in the structures Nano-Ia, Nano-IIa, Nano-IIa derivatives, which is transversal to the nanotube external surface, occurs through the Si atom (Scheme 1), while when the oligomer is linked longitudinally it takes place through a carbon atom belonging to the oligomer (Nano-Ib, Nano-IIb, Nano-IIIb) (Scheme 1). It can be said that there is a compromise between the polarization and electronic delocalization that is

Scheme 1. The CNT-oligomer linking types for all hybrid compounds studied here. To make easier the visualization the CNT was represented by a flat portion of its surface.
needed to achieve the enhancement of $\beta_{\text{mol}}$ for this nonlinear material, as have been also observed for other classes of nonlinear materials [27,46]. The link of donor–acceptor pairs for different classes of compounds have been one efficient strategy for the increasing of $\beta$ magnitude as demonstrated experimentally and theoretically by several research groups [27–31].

Some monosubstituted aniline oligomers with the dicyanovinyl strong acceptor show very high values of $\beta$ according to AM1/TDHF (Austin Model 1 (AM1)/time-dependent Hartree–Fock approach (TDHF)) theoretical calculations [29]. The introduction of this electron-acceptor group increases the polarization since aniline oligomers are electron-donor as observed experimentally [48]. Several molecules containing the dicyanovinyl group show large charge transfer bands that contribute for the large nonlinearities observed in different compounds [49]. Moreover, multiple electron excitation channels as well as charge delocalization in CNT's can participate in the mechanism of high-order harmonic generation. It must be emphasized that the introduction of different nonlinear chromophores ($D$ and $A$ groups) on carbon nanotubes should modify the spectroscopic properties of the hybrid material, therefore the model systems investigated can be utilized at selected wavelengths for applications in different spectral ranges.

The ground state dipole moment values (see Table 1) of the $D$–$A$ nanotube derivatives investigated as well as the ones having only the acceptor (or donor) group attached to the oligomer linked longitudinally or transversely to the CNT are comparable in magnitude with the respective calculated value for the isolated substituted oligomer. The non-substituted CNTs have a null dipole moment value. For the nanocomposites with large dipole moment a charge separation in the ground state should be observed. Therefore, the presence of the oligomer in all designed derivatives contributes to the enhancement of the dipole moment in comparison with the non-substituted nanotube. Hence, it can be envisioned applications for these nanocomposites via poling field.

For the linear polarizability an interesting behavior is observed. It can be seen that all derivatives showed increased values of $\chi_{\text{avo}}$ if comparing with the non-substituted nanotube or to the isolated non-substituted and di-substituted oligomers. In fact, the $\chi_{\text{avo}}$ value for each nanocomposite structure is approximately the sum of the individual values for the corresponding substituted oligomer and free nanotube. In particular, the Nano-IIa exhibits the largest values of $\chi_{\text{avo}}$ among all derivatives, which is the system with the propyl-dicyanovinyl oligomer linked transversely to the nanotube. Therefore, the donor–acceptor pair polarizes the system more efficiently than when only one acceptor or donor group is used. Also, the derivative Nano-IIb with the mono-substituted oligomer longitudinally linked to the external of nanotube surface, having only the phenylamine strong donor group attached to the oligomer end, and IIIa which is di-substituted and linked transversely to the nanotube, show a very large polarizability value, comparable to the Nano-IIa structure.

4. Conclusions

In this work DFT calculations of static first hyperpolarizability for various oligomer–CNT composite structures with electron donor and acceptor substituent groups attached at the ends of the diethynylislane (PDES) decamer using the B3LYP functional and 6–31G(d) basis set were carried out. The oligomer was introduced longitudinally and transversely on the CNT external surface. The link of a $\pi$-conjugated polymer having very enhanced $\beta$ values to carbon nanotubes results in potential nonlinear nanocomposites of second-order response. The largest value of the first hyperpolarizability calculated at the B3LYP/6–31G(d) level for the transversely linked oligomer-CNT structure Nano-IIa was $21991 \times 10^{-30}$ cm$^3$ esu$^{-1}$, undoubtedly a stimulating remarkable value of $\beta$. It was observed that the effect of the interaction of the substituted oligomers with the CNT depends strongly on the nature of the donor–acceptor groups attached to the oligomer end and also on the spatial disposition of the nanocomposite.

The $\beta$ values of the nanocomposites do not differ substantially from the corresponding free oligomer respective values and so, oligomer–CNT composites exhibiting high values of first hyperpolarizability can be designed by choosing adequately a oligomer with very large value of $\beta$. It can also be seen that the free substituted oligomers acquires substantial conduction capacity through the interaction with the nanotube, with the energy gap found lower than 1 eV. Furthermore, the extraordinary properties of CNT associated to the PDES oligomers contribute to relevant properties of these hybrid materials. In special, it can be envisioned applications in the nonlinear field since the values obtained of the first hyperpolarizability are very large in comparison with other nonlinear materials. Further enhancement of the nonlinear coefficient can be achieved by the introduction of stronger nonlinear chromophores in the carbon nanotubes. Also, the number of moieties introduced can be augmented to increase yet more the asymmetry, and hence the magnitude of $\beta$. The present work demonstrated that derivatives of carbon nanotubes are prominent candidates as nonlinear second-order materials, besides of the already well known property as the third-order material.

A very important result of this work is the remarkable trend in the calculated B3LYP/6–31G(d) $\beta$ values for the nanocomposites as compared with the free oligomers. Our results strongly indicates that no matter the level of calculation employed for the evaluation of the first hyperpolarizability the $\beta$ value for the oligomer-CNT composite structures tend to be comparable to the respective value for the free oligomer. If the level of theory and basis set are changed the absolute value of $\beta$ can be larger or smaller, but the effect would be the same for composite and free oligomer structures. Therefore, it can be expected that the procedure of adding an oligomer to a CNT will certainly produce a composite material with non-linear response similar to the free oligomer, what is a welcome result.

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