Third-order nonlinear optical response and optical limiting of colloidal carbon dots

Panagiotis Aloukos,¹,² Irini Papagiannouli,¹,² Athanasios B. Bourlinos,³,⁴ Radek Zboril,⁴ and Stelios Couris¹,²,*

¹Department of Physics, University of Patras, 26504, Patras, Greece
²Institute of Chemical Engineering Sciences (ICE-HT), Foundation for Research and Technology-Hellas (FORTH), 26504, Patras, Greece
³Physics Department, University of Ioannina, Ioannina 45110, Greece
⁴Regional Centre of Advanced Technologies and Materials, Faculty of Science, Department of Physical Chemistry, Palacky University, Olomouc 77146, Czech Republic
*couris@physics.upatras.gr

Abstract: In this work, the nonlinear optical response of some organophilic and hydrophilic carbon dots derived from gallate precursors is studied under 4 ns and 35 ps, visible (532 nm) and infrared (1064 nm) laser excitation conditions by the Z-scan technique. The prepared carbon dots were found to exhibit considerable nonlinear optical response in the visible, the organophilic ones exhibiting stronger response in the infrared and, in general, significantly larger response than their hydrophilic counterparts. In all cases, the corresponding nonlinear optical parameters have been determined. In particular, it was found that both carbon dots exhibited important negative nonlinear refractivity, under all excitation conditions tried, corresponding to self-defocusing, while negligible nonlinear absorption was found in the ps regime. Oppositely, both types of carbon dots were found to exhibit sizeable nonlinear absorption under ns excitation, indicating their potential for optical limiting applications. The present results are discussed and compared with other results concerning similar carbon based nanostructures reported in the literature.

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1. Introduction

The carbon dots or C-dots constitute a new class of carbon based nanoparticles, as fascinating as the other nano-carbons, as e.g. fullerenes, nanotubes, graphene etc. The C-dots are discrete carbon particles like e.g. the nanodiamonds. However, being almost spherical in shape and having dimensions no more than 10 nm, the C-dots are fundamentally different from other nano-diamonds [1]. More significantly, they are characterized by a higher ratio of sp$^2$ to sp$^3$ bonding, they have a crystalline or amorphous graphitic core, while, in addition, they show important surface functionalization properties [2]. Perhaps the most exciting feature of the C-dots is their photoluminescent (PL) properties, the theoretical interpretation of which was an enigma when they were originally observed [3]. According to several studies, the photoluminescence arises from the radiative recombination of excitons at surface energy traps [4]. The peak and amplitude of the multicolor emission of the C-dots in the visible can be tailored by the excitation wavelength, the size, the synthesis method and the functional groups covering their surface [5]. Further properties of C-dots have been investigated including photo-induced electron transfer and redox properties [6] and biocompatibility [7]. A revision on the synthetic routes and properties of the C-dots is given in [8].

However, the nonlinear optical (NLO) properties of the C-dots have not attracted much attention so far. In fact, most of the investigations appeared so far, concerning these few nm-sized carbon nanoparticles were mainly focused on their optical limiting action [9–12], since the featureless absorption spectrum of carbon offers unique broadband optical limiting possibilities. The optical limiting (OL) of carbon nanoparticles has been attributed to nonlinear scattering of the incident laser radiation [10–13]. This mechanism is induced by solvent nano-bubbles or micro-plasmas, the origin of both attributed to the heating of the carbon nanoparticles followed by the evaporation of the solvent [14]. Although these phenomena can be well described and simulated [15], they depend in a complex relation on several macroscopic parameters, as laser pulse duration and fluence, beam waist, laser repetition rate and the solvent itself. Few reports have investigated the intrinsic nonlinear absorption and refraction properties of the C-dots or nanoparticles up to now [16,17] attempting to relate them with the underlying physical mechanisms.

From a theoretical viewpoint, electrochemical luminescence (ECL) studies on C-dots suggest an energy structure similar to that of semiconductor nanocrystals [18]. This structure includes core states and surface states. The ECL emission peak is red-shifted with respect to the PL emission peak, the corresponding shift indicating that the emitting states are different. The PL process is attributed to core-states transitions while the ECL process to surface states transitions. In particular, the PL emission from C-dots is sensitive on the passivation of their surface by organic moieties, the latter serving for the stabilization of emissive surface energy traps. This behavior is similar to the inorganic semiconductor quantum dots or nanocrystals, the photoluminescence of which varies upon the surface ligands or semiconductor shells surrounding their core [19–21]. It is interesting to mention that these last factors have been found recently [22–24] to affect significantly the NLO response of these classes of materials.
In analogy to their inorganic counterparts, C-dots are expected to exhibit NLO properties significantly dependent on surface passivation and the nature of the organic moieties used, the size and perhaps the synthetic routes as well [25, 26]. So, it is among the motivations of the present work to investigate in detail the nonlinear optical properties of these nm sized carbon nanostructures, gaining insight into their NLO response and optical limiting action and correlating it with their physicochemical characteristics. Towards these goals the investigated C-dots have been prepared following specific synthetic routes and were completely characterized by several characterization techniques. In particular, two types of C-dots have been prepared, namely organophilic (codenamed LG27) and hydrophilic (codenamed GU5). The former type of dots were derived by mild thermal treatment of lauryl gallate and described in detail elsewhere [27], while the latter ones have been derived by the microwave heating of a gallate/urea precursor and described in detail in the Appendix. For both types of C-dots, a detailed study of their NLO response has been undertaken using Z-scan technique, employing visible (532 nm) and infrared (1064 nm), 35 ps and 4 ns laser pulses.

2. Experimental

The NLO response of the C-dots was investigated by means of the Z-scan technique [28], which allows for the simultaneous determination of the sign and the magnitude of the nonlinear absorption and refraction of a sample from a single measurement [29, 30]. In this technique, the sample is translated along the propagation direction (i.e., the z-axis) of a focused laser beam experiencing thus different laser intensity at each z position. Then, two types of transmission measurements are performed, the so-called “open-” and “closed-aperture” Z-scans, while from their division, the “divided” Z-scan can be obtained. During the former measurement, the sample transmission is obtained, as a function of sample z-position, by measuring the transmitted laser light just after the sample. Then, the nonlinear absorption coefficient $\beta$ can be determined by fitting the “open-aperture” Z-scan transmission curve with the following relation:

$$T = \frac{1}{\sqrt{\pi}} \frac{\beta L_0 L_{\text{eff}}}{1 + z^2 / z_0^2} \int_{-}\ln \left[ 1 + \frac{\beta L_0 L_{\text{eff}}}{1 + z^2 / z_0^2} \right] \exp \left( -t^2 \right) \, dt$$

where $T$ is the normalized transmission, $L_{\text{eff}} = \left[ 1 - \exp(-\alpha_0 L) \right] / \alpha_0$ is the effective sample thickness, $\alpha_0$ is the linear absorption coefficient, $L$ is the sample length, $z_0$ is the Rayleigh length, $z$ is the position of the sample and $L_0$ is the on-axis peak irradiance at the focal plane.

In the latter case, i.e. the “closed-aperture” Z-scan, the transmission of the sample is obtained by measuring the transmitted laser light after it has passed through a small aperture placed at the far field. From the division of the “closed-aperture” Z-scan measurement by the corresponding “open-aperture” one and for weak nonlinear absorption, the “divided” Z-scan can be obtained, from which the nonlinear refractive index parameter $\gamma'$ can be easily determined according to the following relation:

$$\Delta T_{p,v} = 0.406 \left( 1 - S \right)^{0.25} \left| \langle \Delta \Phi_0 \rangle \right|$$

where $\Delta T_{p,v}$ is the total variation of the normalized transmission, $S$ is the aperture linear transmittance, $\langle \Delta \Phi_0 \rangle = k \langle \alpha_0 q_0 \rangle L_{q_{0}}$ is the averaged on-axis phase shift at the focus, $k = 2\pi / \lambda$ is the wave vector, $\lambda$ is the laser excitation wavelength and $\langle \alpha_0 q_0 \rangle = \gamma \langle \phi(t) \rangle$ is the time-averaged refractive index change.

Then, the imaginary and real parts of the third-order susceptibility $\chi^{(3)}$ can be calculated using the following relations [31]:

$$\Delta T_{p,v} = 0.406 \left( 1 - S \right)^{0.25} \left| \langle \Delta \Phi_0 \rangle \right|$$

$\Delta T_{p,v}$ is the total variation of the normalized transmission, $S$ is the aperture linear transmittance, $\langle \Delta \Phi_0 \rangle = k \langle \alpha_0 q_0 \rangle L_{q_{0}}$ is the averaged on-axis phase shift at the focus, $k = 2\pi / \lambda$ is the wave vector, $\lambda$ is the laser excitation wavelength and $\langle \alpha_0 q_0 \rangle = \gamma \langle \phi(t) \rangle$ is the time-averaged refractive index change.

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\begin{align*}
\text{Im } \chi^{(3)} \text{ (esu)} &= \frac{10^{-7} c^2 n_0^2}{96 \pi \omega} \beta \text{ (cm W}^{-1}) \\
\text{Re } \chi^{(3)} \text{ (esu)} &= \frac{10^{-6} c n_0^2}{480 \pi} \gamma' \text{ (cm}^2 \text{ W}^{-1})
\end{align*}

where \( c \) is the speed of light in cm/s, \( \omega \) is the excitation frequency in s\(^{-1} \) and \( n_0 \) is the linear refractive index.

In the present experiments, two different Nd:YAG laser systems were used, namely a 35 ps mode-locked and a 4 ns Q-switched systems, both operating at a repetition rate of 1-10 Hz. The measurements were performed using both the fundamental (1064 nm) and the second harmonic (532 nm) outputs. In order to ensure that no thermal and/or cumulative effects were taking place due to the laser repetition rate, measurements were performed both at 1 and 10 Hz. However, no significant differences were observed in the Z-scans.

The UV-Vis-NIR absorption spectra of the prepared samples were regularly recorded before and after irradiation, to check for any effects arising from the laser radiation, while the samples were often stirred so that the incident laser beam was irradiating always fresh sample material. For the measurements, several concentrations of organophilic (LG27) \[27\] and hydrophilic (GU5) (see e.g. Appendix) C-dots dispersed in chloroform and water respectively were prepared. The samples were placed into 1 mm thick quartz cells. Some characteristic UV-VIS-NIR absorption spectra are shown as an example in Fig. 1.

![Absorption spectra of LG27 in chloroform (a) and GU5 in water (b) C-dots dispersions.](image)

**Fig. 1.** Absorption spectra of LG27 in chloroform (a) and GU5 in water (b) C-dots dispersions.

### 3. Results and discussion

In order to investigate the NLO response of the organophilic and hydrophilic C-dots and determine their NLO parameters (i.e., the nonlinear absorption coefficient \( \beta \) and the nonlinear refractive parameter \( \gamma' \)), the NLO response of neat chloroform and distilled water had to be measured first, since they were found to possess non-negligible NLO response under ps excitation, thus contributing to the NLO response of the dispersions. In Fig. 2(a) and 2(b) the “divided” Z-scan of a 1.7 mg/mL dispersion of organophilic C-dots in chloroform and the corresponding measurement of neat chloroform are presented, both obtained under identical experimental conditions, under 35 ps, 532 and 1064 nm laser excitation. Chloroform was found to exhibit a pre-focal transmission minimum followed by a post-focal maximum at both excitation wavelengths, indicating positive sign nonlinear refraction (i.e. self-focusing), while the corresponding \( \Delta T_{p-v} \) values of the C-dots dispersions were found lower than those of the solvent, indicating that the C-dots had opposite sign nonlinear
refraction (i.e., negative, self-defocusing) for both excitation conditions (i.e., 532 and 1064 nm). Similar Z-scan experiments of hydrophilic C-dots dispersions have resulted to significantly weaker refractive nonlinearity for visible excitation as can be seen in Fig. 2(c), while negligible nonlinear refraction was found under infrared excitation.

Fig. 2. “Divided” Z-scans of organophilic LG27 (a,b) and hydrophilic GU5 (c) C-dots under 35 ps, 532 nm (a,c) and 1064 nm (b) laser excitation.

It is important to note at this point, that the chloroform, the distilled water and both types of C-dots dispersions were all found to exhibit insignificant nonlinear absorption under ps excitation, for both excitation wavelengths, for the range of incident laser intensities employed. In details, under visible excitation, the LG27 dispersions and the chloroform were found to exhibit large NLO refraction for intensities higher than 18 GW/cm² (i.e., ~3 μJ) and weak NLO absorption becoming observable at intensities higher than 60 GW/cm². The distilled water was found to exhibit insignificant NLO absorption and small NLO refraction for intensities higher that 66 GW/cm² (i.e., ~11 μJ). Moreover, under infrared excitation, the LG27 dispersions and chloroform were found to exhibit sizeable NLO refraction for intensities higher than 30 GW/cm² (i.e., ~15 μJ) and measurable NLO absorption only above 90 GW/cm². Correspondingly, the distilled water exhibited negligible NLO absorption and weak NLO refraction only above 80 GW/cm² (i.e., 40 μJ).

Opposite to the absence of NLO absorption observed under picosecond excitation, all C-dots dispersions exhibited sizeable NLO absorption under nanosecond laser pulses. In Fig. 3(a) and 3(b), some characteristic Z-scan recordings of organophilic and hydrophilic C-dot dispersions are presented, obtained using 4 ns, 532 nm laser excitation. As shown, the “open-aperture” Z-scans of the organophilic C-dots exhibited a transmission peak (filled symbols) indicating saturable absorption (SA), while the Z-scans of the hydrophilic C-dots exhibited a transmission valley (filled symbols) indicative of reverse saturable absorption (RSA). The solvents did not exhibit any NLO response for the range of incident laser intensities used.

It is interesting to comment at this point, that in order the hydrophilic C-dots exhibit similar strength NLO response to that of the organophilic ones, much higher laser intensity had to be used. In fact, a 25-fold higher laser intensity was employed in order to obtain the similar magnitude “open-” and “closed-aperture” Z-scans shown in Fig. 3(a) and 3(b), corresponding to two similar concentrations organophilic LG27 and hydrophilic GU5 C-dots dispersions. This finding clearly depicts the large difference in the NLO response between the two types of C-dots, most probably arising from the different surface passivation methodologies followed for their preparation.
A detailed presentation of the determined values of the nonlinear absorption coefficient $\beta$ (m/W), the nonlinear refractive index parameter $\gamma'$ (m$^2$/W) and the third-order susceptibility $\chi^{(3)}$ (esu) of the studied C-dots under both 35 ps and 4 ns, visible and infrared laser excitation conditions, is given in Tables 1 and 2 together with the values of the solvents used and of a 0.8 mg/mL C$_{60}$-toluene solution. The latters have been included in the tables both for completeness and for comparison purposes. As shown, the hydrophilic C-dots did not have measurable NLO absorption under either ps or ns infrared laser excitation, while the organophilic ones exhibited negligible NLO absorption under ps excitation but significant NLO absorption under ns excitation. It is worth to mention here that the organophilic C-dots were found to exhibit systematically significantly larger NLO response under all excitation conditions than their hydrophilic counterparts. Notably, their NLO response in the infrared was found to be at least similar to that observed under visible excitation. This finding combined with the fact that their linear absorbance $\alpha_0$ in the infrared is significantly lower than in the visible, is of considerable importance for potential photonic applications. In fact, sizeable NLO refractive response in combination with weak linear and nonlinear absorption are prerequisites for various photonic devices and applications, as e.g. in the field of telecommunications. Therefore, from this point of view, the organophilic C-dots seem to be promising candidates compared e.g. to fullerenes, the latter exhibiting insignificant NLO response in the infrared spectral region.

Concerning the “open-aperture” Z-scans of the organophilic C-dots, it is interesting to note that they were found to present transmission maximum at low laser intensity (as discussed above), which however was changing to transmission minimum at higher excitation intensity, indicating RSA behavior. This was experimentally confirmed both for visible and infrared ns laser excitation and it is depicted in Fig. 4, where some characteristic “open-aperture” Z-scans of an organophilic C-dot dispersion measured under different incident laser intensities are shown. The onset of this change was determined to be about 3.6 μJ (~89 μW/cm$^2$) for visible excitation and 12 μJ (~110 μW/cm$^2$) for infrared excitation. The solid lines in Fig. 4 correspond to the fitting of the Z-scans by the following intensity dependent absorption coefficient [24, 31]:

$$\alpha(I) = \frac{\alpha_0}{1 + I/I_s} + \beta_{RSA} I$$  \hspace{1cm} (5)$$

where $I_s$ is the saturation intensity at which the linear absorption coefficient drops to half of its initial value (where SA response was occurring), $\beta_{RSA}$ is the nonlinear absorption
coefficient (associated to the RSA behavior) and \( \alpha_0 \) (cm\(^{-1}\)) is the linear absorption of the sample at the laser excitation wavelength. In particular, from the fitting of the “open-aperture” Z-scans (obtained at laser intensities higher than 60 MW/cm\(^2\)) with Eq. (5), the \( I_s \) and \( \beta_{RSA} \) values were determined to be: \( I_s = 30 \text{ MW/cm}^2 \) and \( \beta_{RSA} = 1.2 \times 10^{-9} \text{ m/W} \), for a 2.8 mg/mL LG27 dispersion, while in this case, the \( I_s \) value corresponds to a (negative) nonlinear absorption coefficient \( \beta \cong -\alpha_0 / I_s = -2.7 \times 10^{-9} \text{ m/W} \).

Table 1. Nonlinear refractive index parameter \( \gamma' \), nonlinear absorption coefficient \( \beta \) and third-order susceptibility \( \chi^{(3)} \) values determined under 532 and 1064 nm, 35 ps laser excitation.

| Sample (mg/mL) | \( \gamma' \) (\( \times 10^{-20} \text{ m}^2/\text{W} \)) | \( \beta \) (\( \times 10^{-11} \text{ m/W} \)) | \( \chi^{(3)} \) (\( \times 10^{-15} \text{ esu} \)) | \( \gamma' \) (\( \times 10^{-20} \text{ m}^2/\text{W} \)) | \( \beta \) (\( \times 10^{-11} \text{ m/W} \)) | \( \chi^{(3)} \) (\( \times 10^{-15} \text{ esu} \)) |
|----------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| LG27 (2.8)    | -6.0±1.0                 | 8.0±2.0                  | -7.8±0.6                 | —                         | 10.0±1.0                 |
| LG27 (1.7)    | -2.0±1.0                 | 3.0±1.0                  | -2.4±0.6                 | —                         | 3.4±1.0                 |
| GU5 (5.0)     | -0.9±0.4                 | 1.0±0.4                  | —                        | —                         | —                        |
| GU5 (2.9)     | -0.2±0.05                | 0.20±0.05                | —                        | —                         | —                        |
| C\text{am} (0.8) | —                        | 1.0±0.1                  | 60.0±10.0                | 7.0±1.0                  | +(0.10±0.01)             | 16.0±3.0                 |
| CHCl\text{3} | 33.0±1.0                 | 46.0±1.0                 | 35.0±1.0                | —                        | 49.0±1.0                |
| H\text{2}O    | 9.5±1.0                  | 10.0±1.0                 | 7.5±0.2                  | —                        | 8.5±0.4                 |

Table 2. Effective nonlinear optical parameters and third-order susceptibility \( \chi^{(3)} \) values determined under 532 and 1064 nm, 4 ns laser excitation.

| Sample (mg/mL) | \( \gamma' \) (\( \times 10^{-17} \text{ m}^2/\text{W} \)) | \( \beta \) (\( \times 10^{-10} \text{ m/W} \)) | \( \chi^{(3)} \) (\( \times 10^{-13} \text{ esu} \)) | \( \gamma' \) (\( \times 10^{-17} \text{ m}^2/\text{W} \)) | \( \beta \) (\( \times 10^{-10} \text{ m/W} \)) | \( \chi^{(3)} \) (\( \times 10^{-13} \text{ esu} \)) |
|----------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| LG27 (2.8)    | -1.0±1                   | -1.4±2                   | 160±10                   | -5.2±0.8                 | -2.9±0.5                 | 81±13                    |
| LG27 (1.7)    | -5.2±0.4                 | -8.3±3                   | 90±10                    | -3.8±0.4                 | -1.8±0.2                 | 58±6                     |
| GU5 (5.0)     | -0.76±0.04               | 1.3±0.3                  | 10.4±0.7                 | —                        | —                        | —                        |
| GU5 (2.9)     | -0.50±0.03               | 0.7±0.2                  | 6.4±0.5                  | —                        | —                        | —                        |
| C\text{am} (0.8) | -8.6±1.3                 | -8.0±1.6                 | 131±20                   | —                        | —                        | —                        |
Fig. 4. “Open-aperture” Z-scans of an organophilic LG27 C-dots dispersion (2.8 mg/mL, $\alpha_0 \approx 8$ cm$^{-1}$) under 532 nm, 4 ns laser excitation exhibiting (a) SA at low laser intensity, and (b,c) RSA at higher intensities.

Then, the optical limiting (OL) action of the C-dots dispersions under ns laser pulses was investigated. To that view, the dependence of the transmission of the dispersions on the input fluence (J/cm$^2$) was systematically investigated for both types of C-dots. As an example, the variation of the transmission of an organophilic and a hydrophilic C-dots dispersions versus the laser fluence in the case of 4 ns, 532 nm laser excitation is presented in Fig. 5. In order to facilitate the comparison, the corresponding optical limiting behavior of two C$_{60}$ solutions in toluene, measured under similar experimental conditions, are also shown. The C$_{60}$ solutions were prepared so that to exhibit similar transmittance with the LG27 2.8 mg/mL and the GU5 5 mg/mL dispersions respectively at low input fluencies. As shown, the organophilic C-dots displayed more efficient OL than the hydrophilic ones, in agreement with what was expected from the “open-aperture” Z-scan measurements shown in Table 2, where the former C-dots exhibited significantly larger NLO absorption than their hydrophilic counterparts.

For a more direct comparison of the optical limiting efficiency of the C-dots with that of C$_{60}$, the onset ($F_{\text{on}}$) and the threshold ($F_{\text{thr}}$) values for optical limiting, defined as the value of laser fluence at which the optical limiting begins [32] and the value of fluence at which the...
normalized transmittance reduces to 50% respectively [33], were introduced and are employed. As shown in Fig. 5, the organophilic and hydrophilic C-dots were found to exhibit onset values \( (F_{on}) \) of about 0.3 and 0.5 J/cm\(^2\) respectively, while the corresponding value for a C\(_{60}\)-toluene solution, having 50% linear transmittance at 532 nm, was determined to be about 0.1 J/cm\(^2\), a value clearly smaller than that of the C-dots. However, in terms of OL threshold, the organophilic C-dots dispersions and the C\(_{60}\)-toluene solution were exhibiting similar OL threshold values \( (F_{th}) \) of about 1 J/cm\(^2\). So, the OL efficiency of the organophilic C-dots was observed to be similar to that of C\(_{60}\), as can be seen in Fig. 5. The organophilic LG27 C-dots were found to exhibit optical limiting for infrared (i.e., 1064 nm) laser pulses as well. However, in this case, their optical limiting was clearly weaker than that obtained for visible laser pulses (i.e., at 532 nm). This difference of the OL efficiency is attributed to the lower linear absorption of the C-dots in the infrared. As a result, it can be concluded that the organophilic C-dots exhibit considerably superior NLO characteristics most probably due to the nature of the functional groups surrounding the graphitic shell of the carbon dots, as it will be discussed below.

![Fig. 5. Fluence dependent transmittance of the LG27 (a) and GU5 (b) C-dots dispersions under 4 ns, 532 nm excitation.](image)

C-dots are known to exhibit properties similar to those of quantum dots. For example, the existence of absorption edges in their absorption spectra shows a semiconducting behavior [17]. Moreover, C-dots exhibit photoluminescence [8] and electrochemiluminescence [18] which are properties of semiconductor nanocrystals as well, such as CdSe and CdTe. However, the properties of C-dots depend strongly on their structure in a complicated fashion compared to the quantum dots. Specifically, C-dots are characterized by a graphitic crystalline or amorphous core, predominantly of sp\(^2\) character. Their shell consists of oxidized carbon. The sp\(^2\) domains inside C-dots (e.g., from polyaromatics) in conjunction with the confinement effects due to the low dimensions, result in the appearance of an energy gap [34]. The energy gap of C-dots can be varied by the size and the functionalization groups attached on their surface, affecting accordingly their optical properties. In particular, the size effect is known to be dependent on whether the core is crystalline or amorphous and does not obey the “particle in a box” phenomenon, which is valid in the case of quantum dots [35]. In addition, the functionalization of the surface of C-dots increases the sp\(^3\) hybridization and increases the energy gap [17].

A simple estimation of the optical band gap of the C-dots is possible from the UV-Vis-NIR absorption spectra (e.g. by means of Tauc plot [36]). As a matter of fact, for the LG27 and GU5 C-dots optical band gaps of about 1.8 and 2.2 eV respectively are estimated. The lower band gap of the LG27 C-dots can be explained by the coupling of the lauryl chain to the delocalized states of carbon surface leading to the reduction of the confinement energies.
of excitonic carriers. In fact, the coupling between organic surfactants and CdSe quantum dots has been reported to result in a bathochromic shift of the band gap [37]. Inorganic semiconductors are known to exhibit optical nonlinearities which scale inversely proportional to the optical energy gap [38]. This scaling can in part explain the higher NLO response of LG27 C-dots than that of the GU5. In addition, the better surface passivation of the LG27 C-dots can be regarded as a further reason for the different NLO responses of the LG27 and GU5 C-dots. In particular, fast recombination of free electrons with holes at non-radiative surface states can result in quenching effects, lowering thus the NLO response. In fact, it has been proposed [6] that the photoluminescence of C-dots can be efficiently quenched by the presence of electron acceptors or electron donors in solution, while by passivating the surface by organic or polymeric functional groups the surface states can trap the photoinduced electrons and holes.

Regarding the origins and the physical mechanisms underlying the NLO properties of the C-dots, they can be considered similar to those of quantum dots. So, upon laser irradiation, electrons from the valence band are getting excited to the intermediate states lying in the linear absorption tail, leading to the generation of a large number of free carriers, electrons and holes. These free carriers can be further excited to higher levels within the conduction band by absorbing photons [39]. Similar assumptions have been considered in [17], where the NLO properties and electron relaxation dynamics of some nm-sized carbon nanoparticles were investigated and the bleaching was attributed to the free and trapped carriers. In addition, we consider two basic processes of nonlinear absorption, two-photon absorption (TPA) and sequential or excited state absorption (ESA). As a general rule, TPA occurs when the laser intensity is of the order of GW/cm², achieved by fs or ps laser pulses, while ESA is a fluence-dependent effect. In that respect, under ns laser excitation TPA is less probable to occur, while under ps laser excitation both TPA and ESA could be considered. In any case, the interplay of parameters like absorption cross-sections of ground and excited states, two-photon absorption cross sections, de-excitation lifetimes etc. can explain the NLO responses observed at the different regimes.

Finally, the amount of the sp² bonding which dominates the graphitic nanocrystalline or amorphous core of the C-dots together with the amount of sp³ hybridization at their surface (resulting from the attached functionalization groups) and the increase of the energy band gap are expected to affect seriously the optical properties of C-dots. This makes the comparison of the NLO response of the various carbon nanoparticles a very difficult task, since even when experimental data are available the sp³/sp² ratio remains to large extent undetermined. The situation becomes even more ambiguous when NLO measurements are performed with different duration laser pulses (e.g., ns/ps/fs), at very different excitation wavelengths corresponding to substantially different absorption conditions, using lasers operating from few Hz repetition rates to several MHz, etc. Considering the above restrictions, there are only very few studies dealing with the NLO response of C-dots or other similar carbon-based nanoparticles. So, in a study few years ago, NLO measurements have been performed on some onion-like carbon and ultradispersed diamond nanoparticles using 532 nm, 10 ns laser pulses. The obtained results have revealed strong NLO absorption and negligible NLO refraction, and at higher incident energies important optical limiting behavior due essentially to nonlinear scattering effects [16]. In particular, for concentrations similar to the ones used here (i.e., ~5 mg/mL) the NLO absorption coefficient β of the onion-like nanocarbons and the nanodiamonds were determined to be $2 \times 10^{-9}$ and $0.3 \times 10^{-9}$ m/W, of the same order of magnitude with the values found in the present study and also the material with the largest sp³ bonding exhibiting the largest NLO response. This is an indication that C-dots with more sp² bonding are expected to possess larger optical nonlinearities.
4. Conclusions

In this work, the NLO properties and the optical limiting action of some recently synthesized organophilic and hydrophilic C-dots have been studied in details using picosecond and nanosecond, visible and infrared laser pulses. Both types of C-dots were found to exhibit important NLO response and efficient optical limiting, the organophilic dots exhibiting much stronger NLO response and better optical limiting properties than their hydrophilic counterparts. In addition, the organophilic C-dots were found to possess significant NLO response in the infrared, making them interesting candidates for photonic applications. The observed differences in the NLO response between the two types of C-dots are discussed and are attributed to the different surface passivation effects due to the different nature of the functional groups attached on the surface of the organophilic C-dots. To the best of our knowledge, this is the first detailed investigation on the nonlinear optical properties of carbon-dots prepared from molecular precursors.

Appendix

Synthesis and characterization of GU5 hydrophilic C-dots

Synthesis: 1.7 g gallic acid (Aldrich), 0.4 g NaOH and 3 g urea were dissolved in 10 mL water (gallate/urea = 1:5 molar ratio). The clear solution was placed in a domestic microwave oven (700 W) and heated for 2 min to give a black solid. The solid was extracted by 20 mL water resulting in a deep brown colloidal dispersion. The aqueous colloid was filtered off prior to the addition of 40 mL acetone in order to precipitate the dispersed dots. The precipitate was isolated by centrifugation and washing with acetone prior to drying. GU5 dots are directly dispersible in water at high concentrations (5-10 mg mL\(^{-1}\)) to give ultra stable colloids (\(\zeta = -38\) mV). Elemental analysis for GU5 (% w/w): C, 25.26; H, 3.07; N, 17.55; O, 43.15, Na, 10.97.

Characterization: TEM and AFM verify the formation of quasi-spherical nanoparticles with size 4-12 nm (Fig. 6). The IR spectrum of GU5 displays two sharp peaks at 1600 cm\(^{-1}\) and 1380 cm\(^{-1}\) assigned to the asymmetric and symmetric stretching modes of -COONa as well absorptions due to residual hydroxyl, amine and carbonyl groups (Fig. 7). In line with elemental analysis, X-ray photoelectron spectroscopy (XPS) shows peaks from C1s (282-289 eV, C=C and C-O), N1s (400 eV, C=N), O1s (532 eV, C=O) and Na1s (1072 eV, -COONa) (Fig. 8). The optical spectra of GU5 in water (Fig. 9) are typical of carbon dot nanoemitters, displaying no absorption but continuous wavelength-depended emission in the visible range. A visual demonstration of the luminescent properties of the dispersed dots under a fluorescence microscope is given as insets in Fig. 9.
Fig. 6. TEM (top) and AFM (bottom) images of the GU5 carbon dots (4-12 nm).

Fig. 7. IR spectrum of GU5 in KBr.
Fig. 8. XPS profile of GU5 sample

Fig. 9. Absorption-emission spectra of GU5 in H₂O (0.2 mg mL⁻¹). Inset: aqueous drops showing purple or green fluorescence under a fluorescence microscope (excitation wavelength: 360-370 nm for purple; 460-495 nm for green).
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