



Electronic and optical properties of sulfur and nitrogen doped graphene quantum dots: A theoretical study



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ABSTRACT

Here we present a theoretical study based on density functional theory (DFT) of the electronic and optical properties of graphene quantum dots (GQDs) doped with sulfur and nitrogen atoms. Unlike the actual literature, which focusses mostly in the edge functionalization of GQDs, our report focusses on the effect of sulfur and nitrogen atomic dopants positioned at the center and near the edge of the GQD carbon backbone structure. According to formation energies, we evidence that doping is more favorable for nitrogen than sulfur, and that the near-edge doping is more favorable than center doping. Regarding the electronic properties, there is a clear shift to lower wavelength in the UV–Vis spectra when using the CAM-B3LYP exchange correlation functional, with respect to B3LYP functional for all the structures, showing a better concordance with experimental data. As a general trend, the major transition observed in the nitrogen doped system is situated at higher wavelength, while in the case of the sulfur doped system, the transition is located at lower wavelength when comparing with the undoped GQDs. This observation is also in good agreement with the experimental trend observed for nitrogen and sulfur-doped GQDs for which a redshift and blueshift in the UV–Vis absorption is typically observed respect to the undoped case, respectively. All of this justify the selected methodology for describing the electronic and optical properties of doped GQDs and provide additional insights to correlate with the optical properties observed experimentally.

1. Introduction

Considerable attention has been recently given to zero-dimensional graphene quantum dots (GQDs) due to their unique electronic and optoelectronic properties with promising applications in photovoltaics, supercapacitors, bioimaging and sensors [1–7]. One of the most interesting features of GQDs respect to graphene is the opening of a band gap and strong photoluminescence response due to the quantum confinement effect [1–3]. It has been already demonstrated that the decreasing size of GQDs (< 10 nm) lead to an increment of the band gap [8–10]. The other interesting feature is an increase of doping feasibility, this feature is particularly advantageous for sensing and electrocatalysis applications [11–14]. Most of the experimental methodologies to obtain GQDs usually lead to formation of different chemical functional groups (mainly oxidized), especially at the edges but also at the basal plane [1–14]. However, the GQDs functionalization and doping with other atoms, mainly with nitrogen and sulfur, has been also recently reported showing excellent tuning of the opto-electronic properties [15–22]. However, there is still a great variability of the experimental optoelectronic properties that could be probably associated to the different preparation methodologies of these GQDs doped with nitrogen (N-GQD) and sulfur (S-GQD). For instance, N-GQDs prepared by graphene oxide reduction with N_2H_4 yielded to the formation of NHR-GQDs,

theoretically modeled as edge NH_2 doped GQDs [15]. On the other hand, N-GQDs prepared by the oxidation of NH_3 -treated GO using a modified Hummer's method lead to the formation of N-GQDs evidencing nitrogen atoms as quaternary N, pyridine-like and pyrrole-like N, with maximum optical absorption located at ~ 400 nm [16]. Finally, the hydrothermal synthesis of N-GQDs using citric acid and urea as sources lead to formation of mainly pyrrolic C-N-C groups with a maximum optical absorption at ~ 340 nm¹⁹. In the case of S-GQD, the preparation by graphite electrolysis with sodium p-toluenesulfonate yielded to the formation of S-GQDs with C-S-C at the framework of the GQD structure and oxidized sulfur evidenced by the presence of C-SO₂-C groups, probably at the edge of the GQD structure, showing maximum absorption at ~ 310 nm²⁰. Then, S-GQDs prepared by hydrothermal synthesis using fructose and sulfuric acid also lead to the presence of mixed C-S-C and C-SO₂-C groups, but with maximum absorption at ~ 270 nm²¹. Finally, the hydrothermal synthesis using 1,3,6-trinitropyrene and 3-mercaptopropionic acid yielded to the formation of S-GQDs with the apparent formation of mixed C-S-C and C-SO₂-C groups, and the maximum of the optical absorption was observed at ~ 400 nm²². Although there are recent theoretical approaches by means of Density Functional Theory (DFT) calculations to understand the optoelectronic properties of GQDs [23–25], NH_2 -doped GQDs [15,26] and GQDs interacting with organic molecules [27] the nitrogen and

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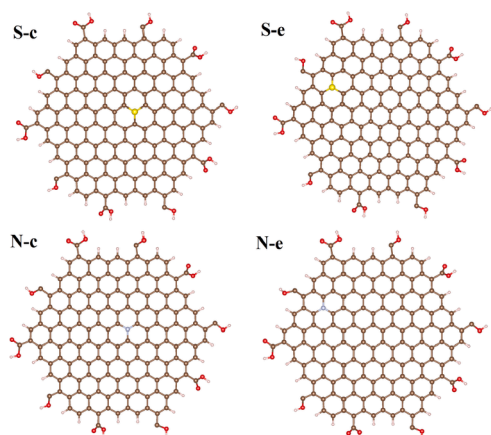


Fig. 1. Top view for S-c, S-e, N-c and N-e structures.

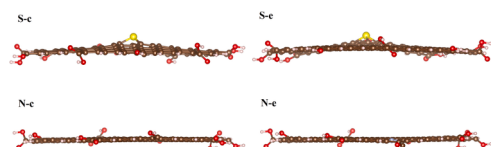


Fig. 2. Side view for S-c, S-e, N-c and N-e structures.

Table 1
Formation energy for all structures.

Structure	E_{form} (eV)
S-c	10.95
S-e	10.40
N-c	4.27
N-e	3.89

sulfur atomic doping at different positions on the GQDs framework has not been theoretically studied yet. The aim of the present report is to shed some light in the possible optical and electronic properties dependence on the nitrogen and sulfur doping of GQDs by means of DFT [28,29] calculations. In particular we utilized two xc-functionals, the conventional B3LYP [31–34] and the modified CAM-B3LYP [37], where the last one has been successfully applied for a better description of electronic excitations (“Time Dependent DFT”) (TDDFT) and charge transfer CT, due to better account of the long-range corrections of the exchange-potential.

2. Methodology

In this report we perform calculations based on DFT [28,29] using Gaussian 09 [30], with the B3LYP [31–34] exchange correlation functional (xc-functional) and 6–31 g(d) basis set for geometry optimizations. In order to obtain optical absorption spectra we proceeded utilizing TD-DFT [35,36] calculations, using the B3LYP xc-functional [31–34] and the long-range corrected CAM-B3LYP [37] functional with 6–31 g(d) basis set, selecting the first 20 singlet-singlet excitations for optical study. The reason for using the CAM-B3LYP xc-functional is to improve the description of charge transfer excitations, while keeping the reasonable description of the atomization energies of the conventional B3LYP xc-functional. All graphene quantum dots were functionalized with –OH and –COOH in the edge as a reference of GQDs and were additionally doped with sulfur (S) or nitrogen (N) near the edge (S-e, N-e) and at the center (S-c, N-c) of the carbon backbone. In all

cases, the backbone of the graphene quantum dots is modeled by 149 carbon atoms. The procedure involved first a structural optimization until reaching a force and energy tolerance of 0.015 eV/Å and 0.023 eV, respectively, and the TDDFT calculations for a fixed geometry, the one obtained in the first structural relaxation.

3. Results and discussion

Top and side view for the edge –OH and –COOH functionalized graphene quantum dots [25,27] with the additional sulfur and nitrogen doping in the center and edge for each case are presented in Figs. 1 and 2, respectively. Formation energies (E_{form}) for all structures were calculated with the following equation:

$$E_{\text{form}} = E_x - (E_{\text{GQD}} - \mu_c + \mu_a)$$

where μ_a is the chemical potential of sulfur or nitrogen atom (defined as total energy per atom), μ_c is the chemical potential of carbon, E_{GQD} the energy of the undoped graphene quantum dot and E_x is the energy of the S-c, S-e, N-c and N-e doped structures. The formation energies are summarized in Table 1. Following the definition of the formation energy, a more positive value indicates a less favorable process, while a more negative value indicates a more favorable process. According to this, the edge doping seems to be more stable than center doping for both sulfur and nitrogen. The nitrogen doped system is more stable than the sulfur doped system. In the case of sulfur doping such atoms are located out-of-plane for both S-c and S-e structures, being in agreement with previous articles [38]. However, for the case of nitrogen doping, the nitrogen atoms are located in-plane for both N-c and N-e structures, as it can be seen in Fig. 2. Carbon-carbon bond length histograms for sulfur and nitrogen doped systems are shown in Fig. 3. All the histograms are similar denoting that the carbon-carbon bond length of the backbone is not affected by the nature of the doping (sulfur or nitrogen) and the position where the doping atom is situated (center or edge).

UV–Vis spectra for undoped, sulfur- and nitrogen-doped GQD systems are shown in Figs. 4–6, respectively; using both B3LYP and CAM-B3LYP xc-functionals, representing with red bars the transitions contributions. All the optical transitions could be described as charge transfer excitations, involving π^* -states ($\pi^* \rightarrow \pi^*$). A shift in the calculated UV–Vis maximum toward lower wavelengths was observed for the undoped GQD system when using the long-range corrected CAM-B3LYP respect to B3LYP xc-functional, as similarly observed previously [23]. In the present case, we evidenced a shift from in the UV–Vis from ~854 to 608 nm when using the CAM-B3LYP xc-functional, which is in good agreement with experimental value observed for GQD (C132) in toluene (~560 nm) [4] but still far from those values experimentally observed for highly oxidized GQD (~300–400 nm) depending on their size, defects and type of oxidized groups [39].

A shift in the UV–Vis spectra between B3LYP and CAM-B3LYP xc-functionals was also observed for the sulfur doped systems, as depicted in Fig. 5, being the maximum absorbance intensity at a lower wavelength for CAM-B3LYP than B3LYP functionals but showing practically the same behavior with both functionals. The S-c system had two absorbance intensity maximums while the S-e system had only one intensity maximum. It is also interesting that the major absorbance of the S-c and S-e systems are located practically at the same wavelength (~580 nm) for CAM-B3LYP functional. The nitrogen doped systems showed a similar behavior for B3LYP and CAM-B3LYP functionals, where the maximum in the UV–Vis absorption is located at lower wavelength for CAM-B3LYP respect to B3LYP functionals. UV–Vis spectra for centered doped systems are more dispersed than for the edge doped systems with maximum absorbance at ~890–1010 nm and 650 nm for N-c and N-e systems, respectively. As a general trend, when comparing nitrogen or sulfur-doped GQDs with the undoped system, the major

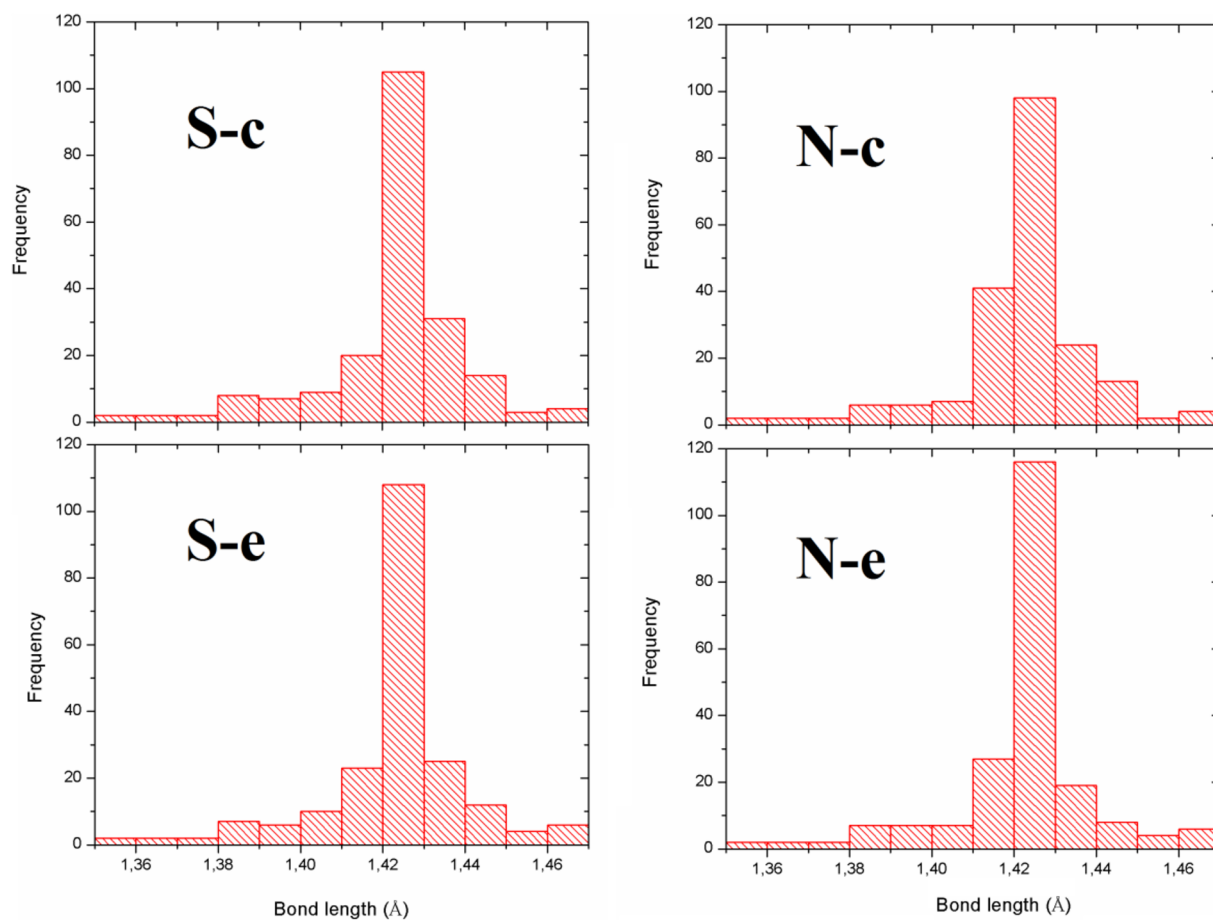


Fig. 3. Carbon-carbon bond length histograms for sulfur and nitrogen doped systems.

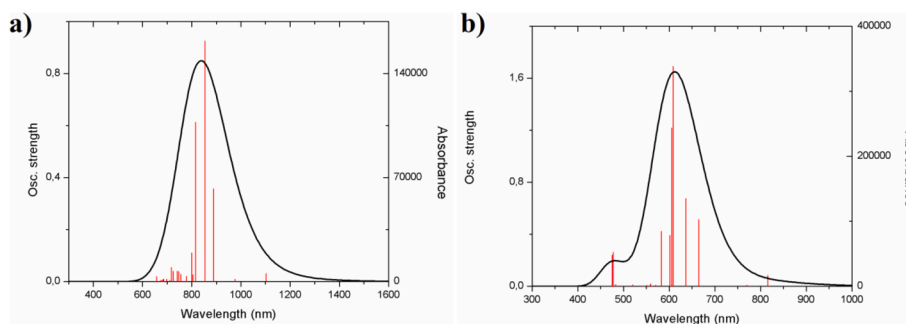


Fig. 4. UV-Vis spectra for undoped GQD system using a) B3LYP and b) CAM-B3LYP functional.

transition observed in the nitrogen doped system is situated at higher wavelength, while in the case of the sulfur doped system the transition is located at lower wavelength. This observation is in good agreement with the experimental trend observed for nitrogen- and sulfur-doped GQDs for which a redshift and blueshift in the UV-Vis absorption is typically observed respect to the undoped case, respectively [16,19–21].

Electronic density differences maps (EDDM) for S-c using B3LYP and CAM-B3LYP functional are shown in Fig. 7. EDDM for S-c shown corresponds with 771.8 nm and 1406.8 nm transitions for B3LYP functional and 577.1 nm and 1032.9 nm for CAM-B3LYP functional. The first transition corresponds to the major peak ascribed to the

UV-Vis spectrum in Fig. 5a and b. The second one is the major contribution of the second distribution of the UV-Vis spectrum. In all the EDDM for S-c structure showed a yellow region around the sulfur, which indicates a loss of electron density in the transition to the excited state. The same behavior is presented in the S-e structure as it can be seen in Fig. 8. The EDDM for N-c are shown in Fig. 9. Near the nitrogen atom doping region, a gain in electron density in a transition to the excited state is observed for B3LYP functional and it is shown in blue color, while for CAM-B3LYP functional there is no evidence for a majority region of gain or loss of electron density. EDDM for N-e are presented in Fig. 10: in this case a yellow zone is observed in the region of the nitrogen doping for both xc-functionals.

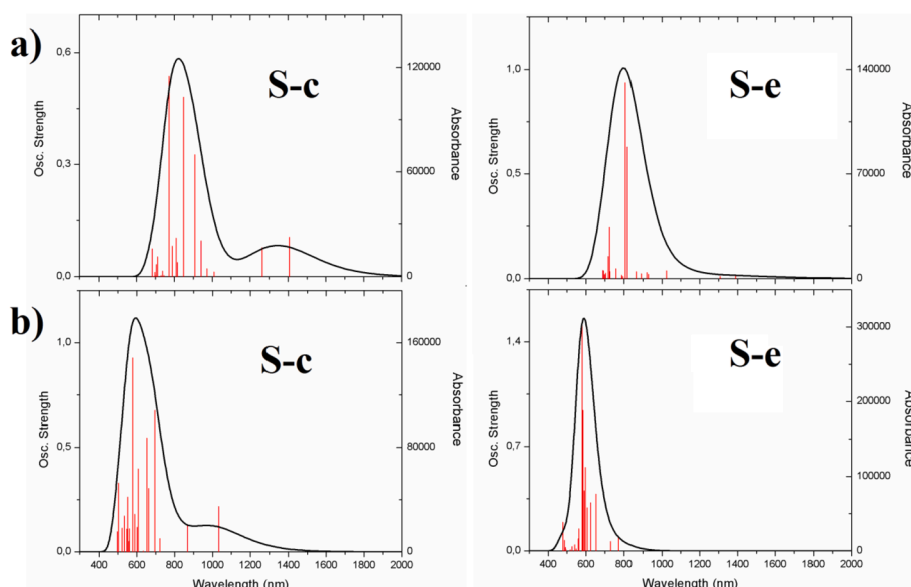


Fig. 5. UV-Vis spectra for sulfur doped system using a) B3LYP and b) CAM-B3LYP functional.

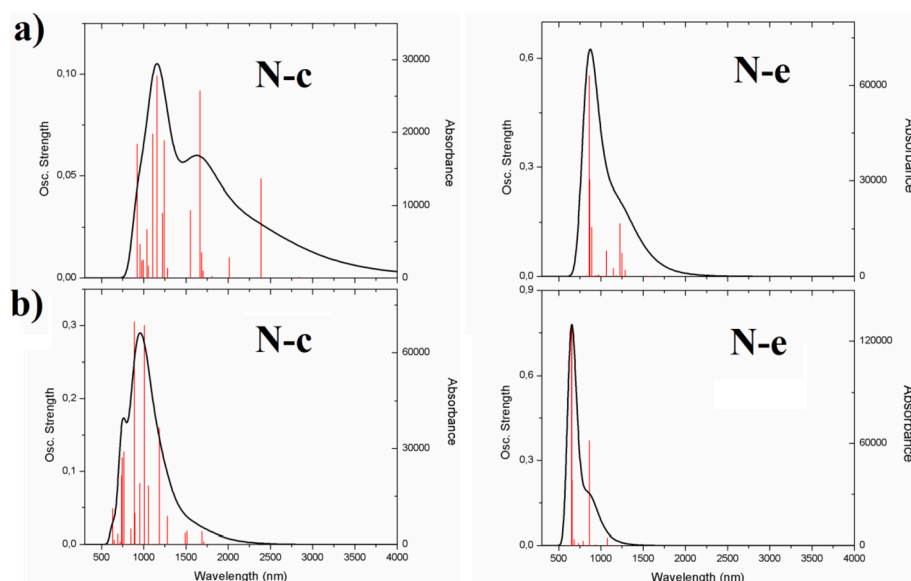


Fig. 6. UV-Vis spectra for nitrogen doped system using a) B3LYP and b) CAM-B3LYP functional.

The major contributions for the most relevant transitions for B3LYP and CAM-B3LYP functionals are shown in Tables 2 and 3, respectively. For sulfur doped systems the HOMO-2→LUMO+1 transition is the most relevant for B3LYP functional, while for CAM-B3LYP functional, the HOMO-2→LUMO transition is the most relevant for S-c system, and HOMO-1→LUMO+1 transition for S-e system. The N-c system presented the highest transition, being HOMO→LUMO+1 and HOMO-1→LUMO for N-e system for B3LYP functional. For the other functional the HOMO → LUMO+4 and the HOMO → LUMO+3 transitions, are the most relevant for centered and edge doped systems, respectively.

4. Conclusions

Graphene quantum dots were doped with a sulfur and nitrogen atom in the center and edge of the carbon backbone. According with the formation energy, it is easier to dope with nitrogen in comparison to sulfur atoms, and the edge doping is more favorable than the centered one. From a structural point of view, the nitrogen atom is more similar in size than the sulfur atom when compared to carbon atoms. Additionally, the centered doping is harder due to the presence of more stress, while the edge doping allow the reordering and reconstruction around of the neighbor atoms, being more effective to the stress release

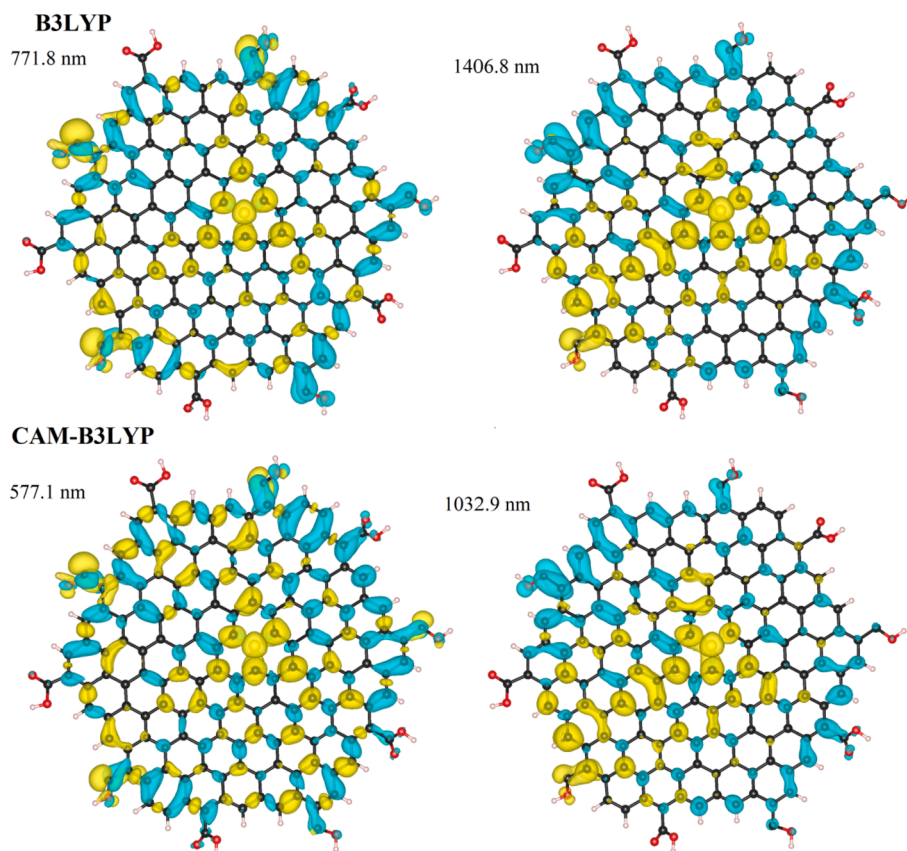


Fig. 7. Electronic density differences maps (EDDM) depicting the most relevant optical transitions for S-c utilizing B3LYP and CAM-B3LYP functional. Yellow regions indicate a loss of electron density in the transition to the excited state and blue regions indicate a gain of electron density in a transition to the excited state.

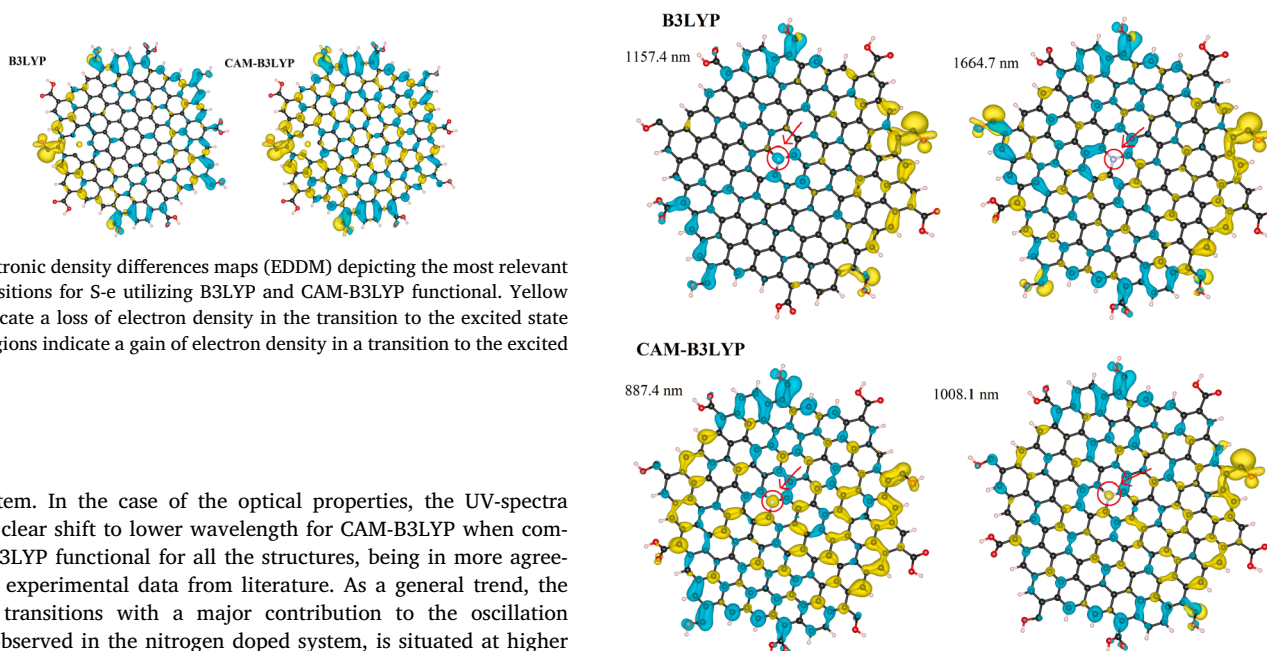


Fig. 8. Electronic density differences maps (EDDM) depicting the most relevant optical transitions for S-e utilizing B3LYP and CAM-B3LYP functional. Yellow regions indicate a loss of electron density in the transition to the excited state and blue regions indicate a gain of electron density in a transition to the excited state.

of the system. In the case of the optical properties, the UV-spectra presents a clear shift to lower wavelength for CAM-B3LYP when compared to B3LYP functional for all the structures, being in more agreement with experimental data from literature. As a general trend, the electronic transitions with a major contribution to the oscillation strength, observed in the nitrogen doped system, is situated at higher wavelength, while in the case of the sulfur doped system the transition is located at lower wavelength, when comparing with the undoped QGDs. According to all these results, there is a better description of the optical properties when utilizing CAM-B3LYP functional for this carbon system.

Fig. 9. Electronic density differences maps (EDDM) depicting the most relevant optical transitions for N-c utilizing B3LYP and CAM-B3LYP functional. Yellow regions indicate a loss of electron density in the transition to the excited state and blue regions indicate a gain of electron density in a transition to the excited state. Nitrogen atoms were indicated with red arrows.

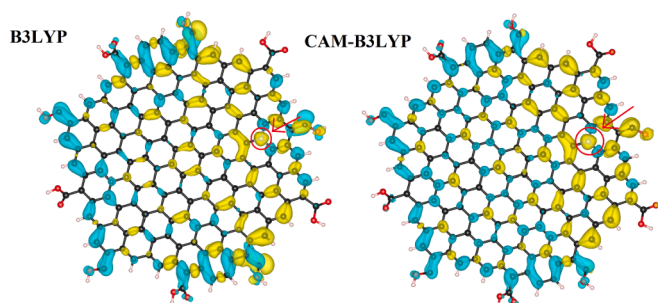


Fig. 10. Electronic density differences maps (EDDM) depicting the most relevant optical transitions for N-e utilizing B3LYP and CAM-B3LYP functional. Yellow regions indicate a loss of electron density in the transition to the excited state and blue regions indicate a gain of electron density in a transition to the excited state. Nitrogen atoms were indicated with red arrows.

Table 2

Wavelength, oscillator strength and major contribution for all structures utilizing B3LYP functional.

Structure	Wavelength (nm)	Oscillator strength	Major contribution
S-c	771.8	0.5374	HOMO-2→LUMO + 1 (24%), HOMO-3→LUMO (19%)
	1406.8	0.1062	HOMO→LUMO (89%)
S-e	806.2	0.9381	HOMO-2→LUMO + 1 (32%), HOMO-2→LUMO (25%)
N-c	1157.4	0.0992	HOMO→LUMO + 1 (34%), HOMO→LUMO (18%)
	1664.7	0.0919	HOMO→LUMO + 3 (25%)
N-e	861.3	0.5523	HOMO-1→LUMO (30%), HOMO-1→LUMO (29%)

Table 3

Wavelength, oscillator strength and major contribution for all structures utilizing CAM-B3LYP functional.

Structure	Wavelength (nm)	Oscillator strength	Major contribution
S-c	577.1	0.9273	HOMO-2→LUMO (26%), HOMO-1→LUMO + 1 (20%)
	1032.9	0.2175	HOMO→LUMO (85%)
S-e	578.8	1.519	HOMO-1→LUMO + 1 (41%)
N-c	887.4	0.3051	HOMO→LUMO + 4 (24%), HOMO→LUMO + 3 (15%)
	1008.1	0.3005	HOMO→LUMO (20%), HOMO→LUMO + 3 (12%)
N-e	654.3	0.7822	HOMO→LUMO + 3 (13%), HOMO→LUMO + 2 (11%)

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