

Full Length Article

Curvature and vacancies in graphene quantum dots

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ABSTRACT

The optical properties and the geometric characteristics of multivacancy graphene quantum dots systems are studied using Density Functional Theory calculations, in a systematic way, in relation to the number of carbon atoms extracted and the relative configurations that could be present in the cluster. The way to characterize these configurations was using the complementary figure model -i.e. the figure formed by the carbon atoms extracted in order that the vacancy could be created-. The number of pentagonal or square figures formed after structure optimization, as well as their relative location, is found to be very relevant to determine the curvature level of the graphene quantum dot, but the occurrence of higher order cycles have a non-negligible role and cannot be ruled out. However, this occurrence is much dependent on the specific multivacancy to be studied and prevents to reach more accurate models that could allow the prediction of the magnitude of the curvature. We found unexpected instability in dendritic-like vacancies and we suggest that the non-periodic character of the graphene quantum dot, in contrast to graphene, would prevent such vacancies to be relaxed in a higher extension, causing this kind of systems to be less stable than, for example, zigzag complementary figures systems.

1. Introduction

In the last years intense research has been carried out on graphene and their properties with the purpose of its use in technological devices [1–3]. One of the tasks to be achieved was the opening of the gap, and one of the procedures to reach that goal was to introduce defects in the graphene layer, in particular through the inclusion of vacancies [4–6].

Experimental techniques to perform vacancies in graphene have been evolving, ranging from methodologies with high control -high technologies demanding, not suitable for series production- to other ones with more random, non-controllable characteristics – closer to the applications as soon as they become improved [7,8].

More recently, graphene quantum dots -GQDs- have arisen as materials with potential interest for technological applications, in electronics, solar cells, sensors, etc. [9–13].

However, due to the top-down methodologies usually performed to achieve their synthesis, it should be accepted that these GQDs most probably exhibit defects, such as vacancies. Due to these non-controlled procedures, it should be unavoidable to get vacancies in the obtained GQDs, caused by the oxidation processes usually used [14–16]. This fact has been usually overlooked.

Although single-, di- and multivacancy systems in graphene have been studied [4–6], the presence of vacancies in GQDs needs still a more comprehensive research. While it is true that graphene and GQDs

have the same nature, the fact that the latter cases are clusters with boundaries and therefore with no constraints beyond their own limits and that graphene is periodic in its 2D structure, gives a difference that it is important and makes it worthwhile to undertake this task.

The purpose of this manuscript is to understand the consequences of the presence of vacancies with different configurations in GQDs.

2. Methodology

In this work we constructed graphene quantum dots (GQD) with the following types of edge chemical functionalization in each GQD: –H, –OH and –COOH, corresponding to the following empirical formula, $C_{160}H_{30}O_{15}$, for the non-vacancy system. Then we proceeded to construct 1–8 order carbon vacancy system with the same type of edge chemical functionalization.

We performed DFT calculations [17,18] utilizing Gaussian 09 [19], selecting the B3LYP [20–23] xc-potential at the 6–31 g(d) level of theory.

The tolerance in total energy was selected to 1×10^{-6} a.u. for both singlet and triplet multiplicities, applying a basis set superposition error (BSSE) correction according to the counter poise correction [24,25]. No restrictions were applied to the point group symmetry of the molecules, allowing full degree of freedom during the geometrical optimization selecting a force tolerance of 3×10^{-4} a.u.

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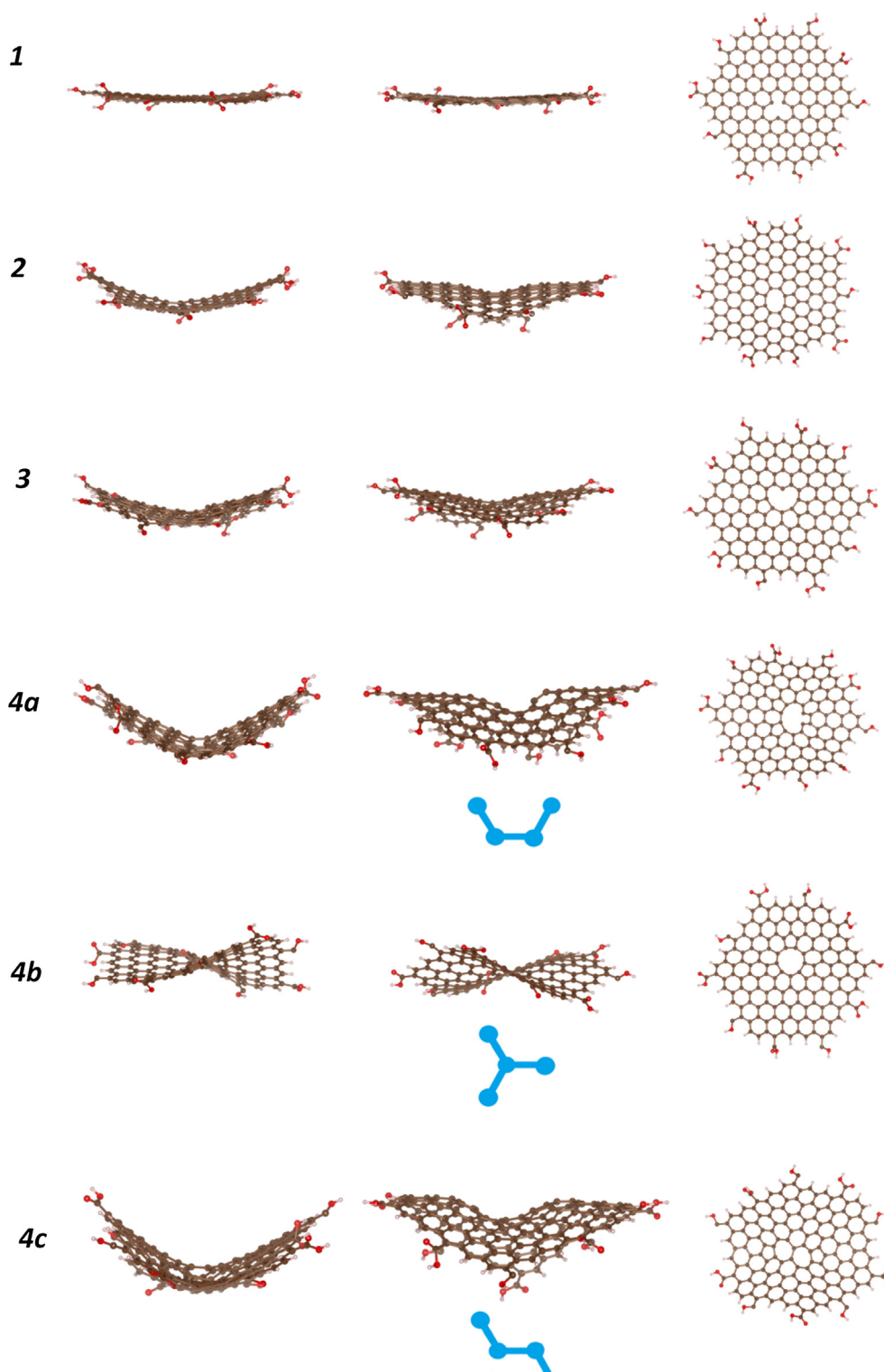


Fig. 1. Side (left and middle) and top (right) view for 1–3, 4a, 4b and 4c structures, with the corresponding complementary figure (down, in blue color) [32]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

For optical study, we utilized the same conditions for the Gaussian09 set up in order to proceed with time-dependent DFT calculations (TD-DFT) [26,27], with the first 20 singlet-singlet excitations.

3. Results and discussion

The scheme of the multivacancy systems studied in this manuscript is shown in Figs. 1–3, where all the vacant systems were allowed to

structurally optimize. The strategy followed was to extract 1–8 atoms from the defined non-vacant model, describing the configuration using the complementary figure, a tool used in previous reports -i.e. the geometric figure of the atomic arrangement that is extracted from graphene when the multivacancy is created- [4–6].

As it was explained in these previous manuscripts, the advantage of this concept is the capability to create complex multivacancy systems in similar configurations as what can be expected to be found

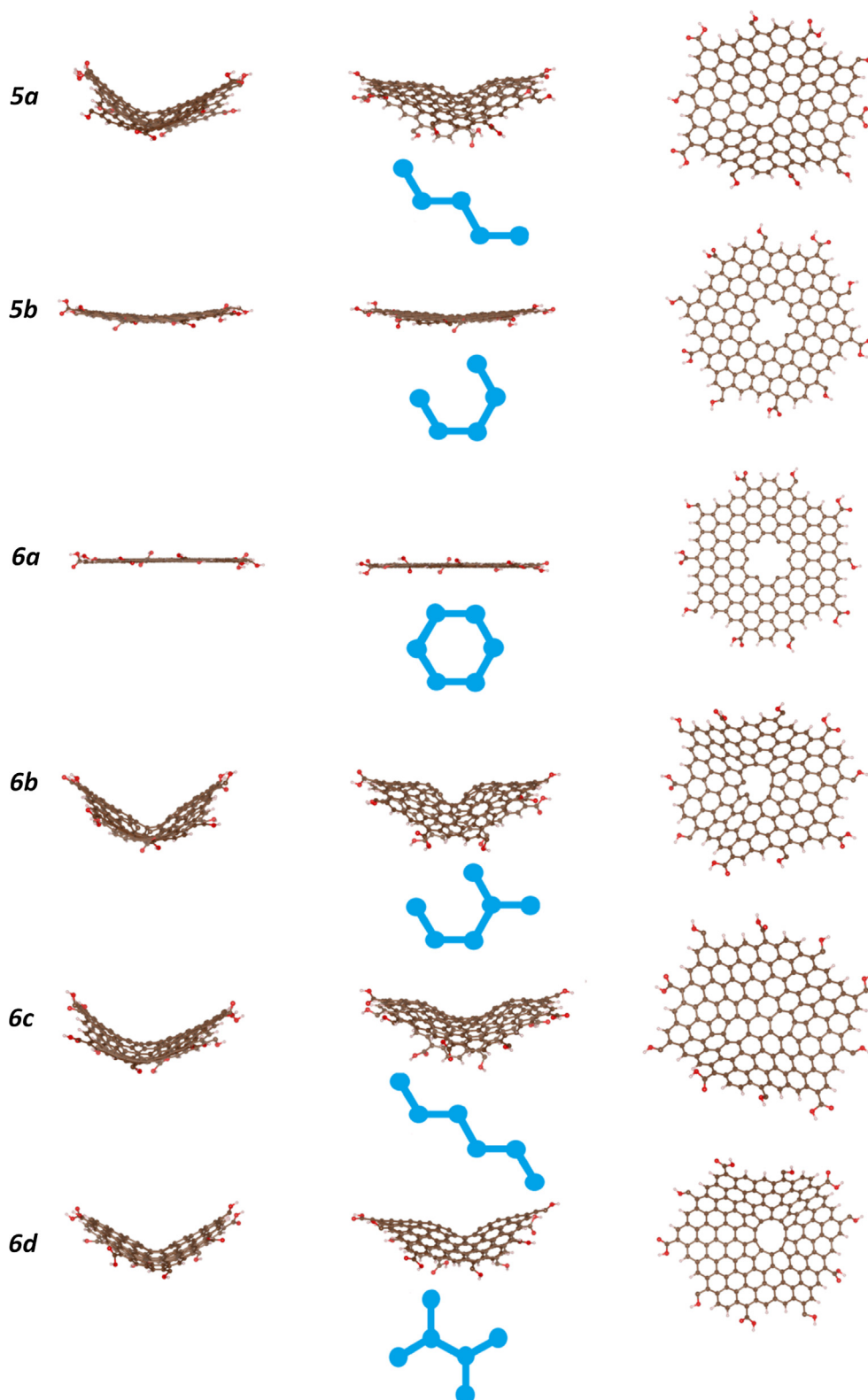


Fig. 2. Side (left and middle) and top (right) view for 5a, 5b, 6a, 6b, 6c and 6d structures, with the corresponding complementary figure (down, in blue color) [32]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

experimentally in non-controlled syntheses, and to allow the optimization in realistic conditions. Additionally this tool is a precise way to unambiguously designate multivacancies with reference of the configuration of the carbon atoms extracted.

In Figs. 1–3 the so-called complementary figures are shown in blue

color for the possible ambiguous cases, i.e. $N \geq 4$, while the carbon atoms for the x-, y- and z-oriented optimized structures can be seen in the usual dark color -red for oxygen and hollow for hydrogen-. In the single-, di- and trivacancy cases, there is only one possible configuration for the vacancy to occur, and for this reason no complementary figure is

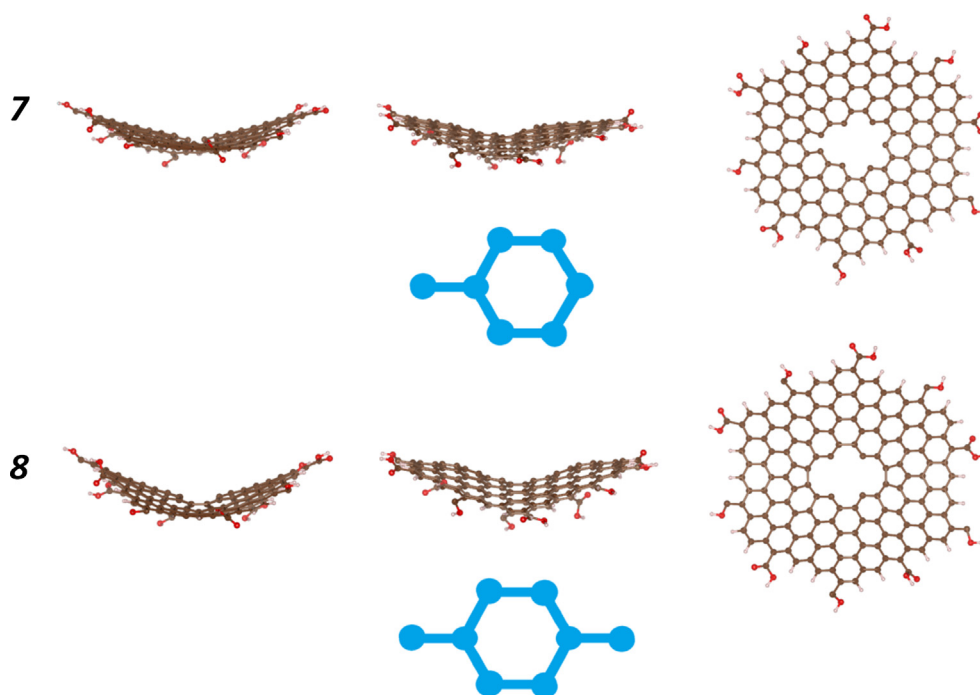


Fig. 3. Side (left and middle) and top (right) view for 7 and 8 structures, with the corresponding complementary figure (down, in blue color) [32]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

shown. This research is focused just on the optimization of the vacant systems disregarding any other rearrangements, such as the case of Stone-Wales defects [28,29]. Even with the exclusion of such cases, this field still shows very complex structures, which are not solely restricted to theoretical simulations but that are being experimentally discovered with the advances in the microscopy techniques that are becoming available for research [8,29,30]. This fact makes this kind of research worthwhile and of interest for fundamental research and potential applications. It is important to mention that Figs. 1–3 show the structures for the most stable multiplicities cases -singlet or triplet-. While the 1, 3, 4b, 6a, 6c and 8 cases were most stable for triplet multiplicity, the 2, 4a, 4c, 5a, 5b, 6b, 6d and 7 cases show more stability for the singlet one.

In spite that the occurrence of ripples was observed for some cases in defected graphene, and the causes of such topological anomalies have been discussed, the curvature of GQDs is still an open topic to study. As it can be seen from these figures -especially in the x- and y-orientations- this effect can be clearly seen in most of the optimized vacant GQDs structures. However and in order to be precise with the terminology, in GQDs cases the 3D distortion is more a curvature rather than a ripple. At this point it is important to quantify the magnitude of the curvature and for this reason, an adequate way could be to use as a starting point the rippling parameter previously defined for graphene, which consists in the largest difference in z-coordinate for the graphene layer [6]. This definition of rippling parameter -curvature parameter for this case-, very useful for graphene, was however not suitable for GQDs, since these clusters have boundaries and the difference in z-coordinate is dependent on how centered the vacancy is. For this reason, in this report, we defined a mean curvature parameter as the difference between the average z-coordinate and the lowest z-coordinate in the GQD.

In order to show the mean curvature parameter for closely related vacancies, Fig. 4 exhibits its dependence with the order of carbon extracted for zigzag complementary figures. The red curve is a third order polynomial fit where $R^2 = 0.995$.

The vacancy created when each complementary figure was extracted from the original GQD, yields to the formation of pentagonal figures after optimization, as well as higher order cycles. The optimization followed the rules established for multivacancies in graphene

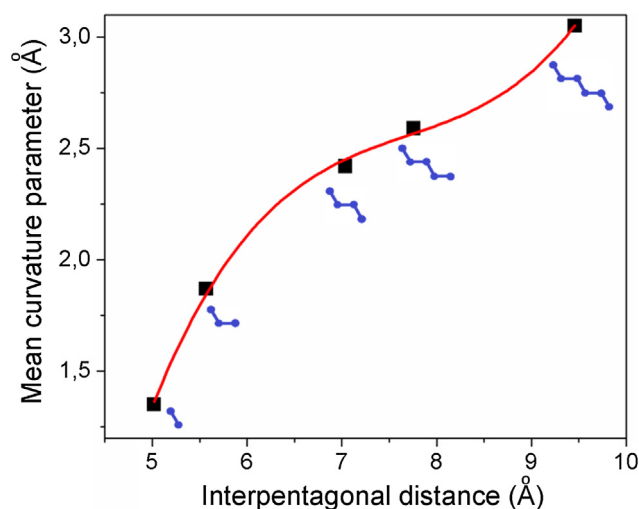


Fig. 4. Mean curvature parameter versus interpentagonal distance for zigzag complementary figures.

that were previously reported [4], with the particular features that appear when a competence of strain is present for special and more complex cases [5]. In particular, the presence of pentagonal figures and the curvature that they cause, have been identified as playing a key role with the ripples found in some cases of multivacant graphene [6] and for this reason it should be relevant to study the curvature in the multivacant GQDs present in this report in relation to the pentagonal figures formed after optimization. Table 1 shows data about the different systems, with particular emphasis on the relation between the mean curvature parameter and the pentagonal figures -number and distances between them-. The number of pentagonal figures should be relevant in the magnitude of the curvature of the multivacant GQD, taking into account that these systems have boundaries and that they are not periodic -i.e. different to similar graphene systems-, and the correlation of the ripples in multivacant graphene and the distances between such figures has been proven, so it is reasonable that it is

Table 1

Mean curvature parameter, number of pentagonal figures after optimization and interpentagonal distances for all structures – bold font stands for distances involving square figures and * for zigzag complementary figures.

N type	Mean curvature parameter (Å)	Number of pentagonal figures after optimization (X)	Interpentagonal distances (Å)	Weighted interpentagonal distances (Å)**
1	0.58	1	–	–
2	1.35	2	5.02*	3.35
3	1.87	2	5.36*	3.58
4a	2.41	3	4.01	4.48
			4.70	
			4.73	
4b	3.08	3	5.01	5.06
			5.03	
			5.13	
4c	2.42	2	7.04*	4.69
5a	2.59	2	7.76*	5.17
5b	0.69	1	–	–
6a	0.17	1	–	–
6b	2.73	4	1.96	6.06
			4.45	
			4.78	
			4.86	
			5.16	
			6.06	
6c	3.05	2	9.32*	6.22
6d	3.19	4	3.93	6.74
			3.96	
			4.93	
			4.94	
			6.27	
			6.28	
7	1.69	1	–	–
8	2.06	2	9.22	6.15

** Calculated from the average value of interpentagonal distances and following the equation described in the text.

another parameter to be studied for the defected GQDs.

While Fig. 5 shows the evolution of the interpentagonal distances with the order of the vacancy for zigzag complementary figures, a distorted staircase curve can be seen. The inset figure makes this fact evident. In previous reports a similar behavior has been observed for nanotubes [31] and graphene [5], but for formation energy for carbon

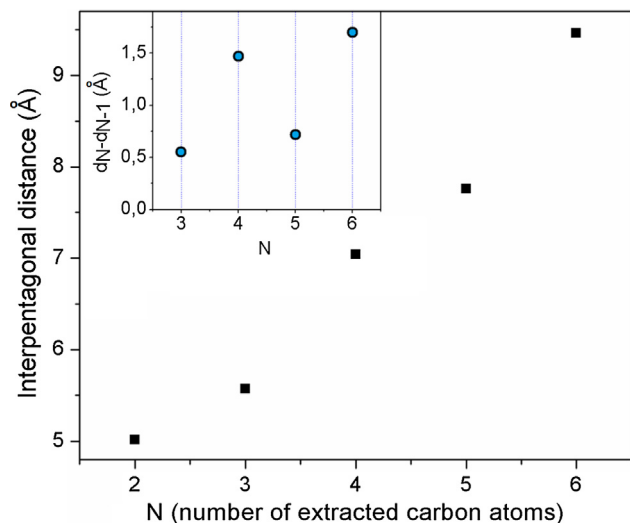


Fig. 5. Interpentagonal distance versus number of extracted carbon atoms (N). The inset figure shows the differences in the interpentagonal distances between successive order (number of extracted carbon atoms), where the staircase shape is evident.

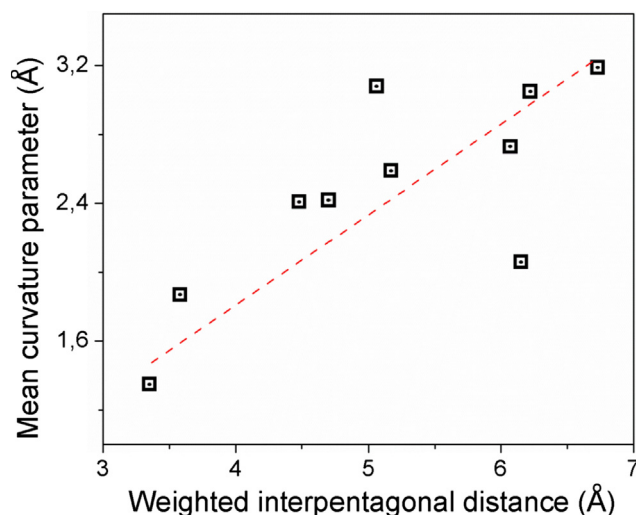


Fig. 6. Mean curvature parameter versus weighted interpentagonal distance. The dotted red line is just a guide to the eye to show a trend. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

atom, not for defect distances, which makes this fact not particularly related, especially taking into account that the higher step for energy in those reports is from the even to the odd order while in this case is from the odd to the even one.

Fig. 6 shows the mean curvature parameter with a weighted interpentagonal distance, defined with these parameters in mind -number and interpentagonal distance-: $D = X\bar{D}/3$, where D is the weighted interpentagonal distance, X is the number of pentagonal figures in the multivacant GQD system and $\bar{D}$ is the average interpentagonal distance for the specific system. For this equation, the normalization was performed for systems with X = 3 -i.e. a triangular-like pentagonal configuration-. In order to determine X and the interpentagonal distances, square configurations were assumed as pentagonal: this fact can be seen in Table 1, where the bold font indicates their participation. Although the dotted red line in Fig. 6 is just a guide to the eye, it is evident that there is a trend and that further improvements to a model should be very complex and dependent on each particular case, since higher order cycles also include curvature to these multivacant GQDs systems. As an example the dihedral angle at the edge shared by two heptagonal in the 4c case is 24.8°. Thus, it is not possible to achieve a general model, because the occurrence and relative configuration of higher order cycles which could contribute to the curvature of the defected GQDs, are specific for each case.

It is possible to conclude the importance of the pentagonal figures, how many they are and the relative configurations between them, although we know that some other important factors should be considered.

Fig. 7 is an analysis of the formation energy shown in Table 2. In the case of the zigzag complementary figures, shown as black upside down triangles, a steady increase in energy is seen with the order of the vacancy. As previously mentioned and similarly to graphene, a staircase form is observed, where the higher steps can be seen from even to odd vacancy orders. This effect can be characterized in the inset figure, where the difference $E(k) - E(k-2)$ follows a similar trend to what was previously observed for graphene [5].

The cases with pro-cycling complementary figures show higher formation energy in comparison to the zigzag complementary figure ones in agreement with the equivalent study in graphene [5].

However, the 4b and 6d cases have surprisingly higher formation energies in comparison to the zigzag complementary figures ones. These cases, with dendritic-like growth, have been considered as the more stable configurations when created on a single-layer graphene

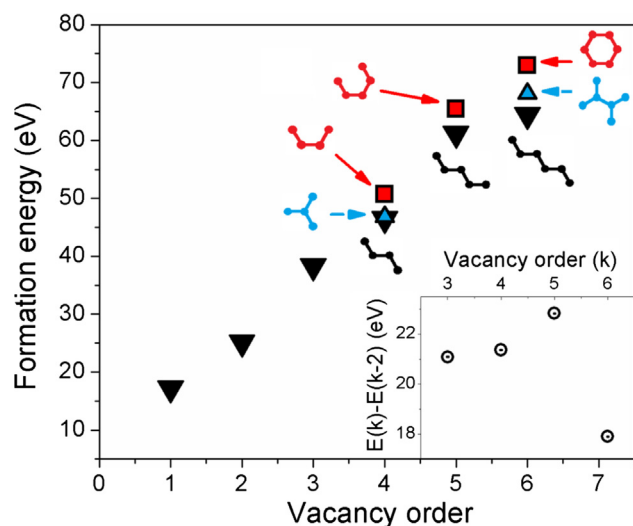


Fig. 7. Formation energy versus vacancy order. Zigzag, dendritic and pro-cycling complementary figures are represented with black triangles, light blue triangles and red square shapes, respectively. Inset shows the difference in formation energies between alternating orders for zigzag complementary figures. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Band gap and formation energies for all structures.

Structure	Orbital (eV)	Band gap (eV)	Formation energies (eV)
No vacancy	LUMO –3.30 HOMO –4.69	1.39	–
1	LUMO –3.91 HOMO –4.56	0.65	17.21
2	LUMO –3.61 HOMO –4.73	1.12	25.10
3	LUMO –4.07 HOMO –4.49	0.42	38.30
4a	LUMO –3.31 HOMO –4.82	1.51	50.71
4b	LUMO –4.01 HOMO –4.41	0.40	46.85
4c	LUMO –3.58 HOMO –4.62	1.04	46.47
5a	LUMO –3.80 HOMO –4.63	0.83	61.14
5b	LUMO –3.98 HOMO –4.77	0.79	65.42
6a	LUMO –4.15 HOMO –4.85	0.70	72.96
6b	LUMO –3.88 HOMO –4.64	0.76	73.29
6c	LUMO –3.73 HOMO –4.28	0.55	64.37
6d	LUMO –3.74 HOMO –4.69	0.95	68.05
7	LUMO –4.07 HOMO –4.79	0.72	85.55
8	LUMO –4.09 HOMO –4.61	0.52	92.58

Formation energies were calculated following: $E_{\text{FORM}} = E_{\text{vac}} - (E_{\text{novac}} + nE_{\text{C}})$, being E_{vac} the total energy for the structure with vacancy, E_{novac} the total energy for the structure without vacancy, n the number of vacancy and E_{C} the total energy for carbon.

matrix [5]. In that previous report, the absence of dangling bonds in the multivacancy graphene systems when these dendritic complementary figures are extracted, was found to be the most relevant cause for this special stability. Moreover, the instability that the presence of dangling bonds in the vacancy is once again emphasized with the pro-cycling complementary figures cases -named 4a, 5b, 6a-. We found that the

Table 3
Wavelength, Oscillation strength, and major contribution for 1, 2, 3, 4a, 4b and 4c.

	Wavelength (nm)	Oscillation strength	Major contribution
1	877.3	0.4652	HOMO-1 → LUMO + 2 (39%) HOMO-2 → LUMO + 1 (33%)
	910.4	0.2787	HOMO → LUMO + 3 (46%)
2	838.0	0.4241	HOMO → LUMO + 2 (66%)
	808.6	0.4071	HOMO-1 → LUMO + 2 (45%)
3	893.9	0.2807	HOMO-1 → LUMO + 2 (45%)
	1102.9	0.1092	HOMO-1 → LUMO + 1 (34%)
4a	804.8	0.1608	HOMO-1 → LUMO + 2 (41%)
	739.7	0.112	HOMO-1 → LUMO + 4 (42%)
4b	1175.3	0.1319	HOMO-1 → LUMO + 1 (39%)
	1210.5	0.1121	HOMO → LUMO + 2 (55%)
4c	832.2	0.1834	HOMO-1 → LUMO + 2 (32%)
	890.2	0.1593	HOMO-4 → LUMO (51%)

reason for the exception of the dendritic cases and their unexpected instability could be due to the absence of a periodic structure -i.e. graphene- with the possible strain relief that an extended structure could allow, but rather exhibiting the high concentration of non-six-membered cycles in a small cluster, which could yield to non-favorable configurations in comparison with the equivalent cases in graphene.

Table 2 shows the band gaps at the time dependent DFT (TD-DFT) level for the structures reported in this manuscript. While the band gap of the non-vacancy system is in the infrared zone (1.39 eV), the single-, di- and multivacancy systems shift their band gaps to even lower energies, to the short-wavelength infrared region. Tables 3 and 4 show wavelength, oscillation strength and major contribution for the transitions to the calculated absorbance spectra, what can be seen in Figs. 8 and 9. The absorbance of all structures is mainly in the infrared region -7 and 8 order vacancies cases show a shift in the absorbance to higher wavelength-. It is clear that the carbon vacancy degree and type of complementary figure changes the electronic structure. As it can be observed in Fig. 10, there is an important contribution for the electronic structure in the region of the vacancies and the cycles formed after structure optimization, for the $N = 1$ and 2 cases -these ones follow the exponential decay trend- and also for $N = 3$ and 5 (i.e. 5a, with zigzag complementary figure). These two cases have in common the presence of a high order cycle: the case $N = 3$, shows a ten-membered ring and the $N = 5$ one, a nine-membered ring, in this case, with an adjacent seven-membered ring (in Fig. 11 they are shown as A, B and C, respectively). These two rings, the ten- and the nine-membered ones, are very similar in their shape (heart-like shape) and, as it can be observed

Table 4
Wavelength, Oscillation strength, and major contribution for 5a, 5b, 6a, 6b, 6c, 6d, 7 and 8.

	Wavelength (nm)	Oscillation strength	Major contribution
5a	957.2	0.3211	HOMO → LUMO + 2 (59%)
	1215.5	0.1376	HOMO-1 → LUMO + 1 (36%)
5b	1194.5	0.033	HOMO-4 → LUMO (37%)
	907.9	0.0269	HOMO-1 → LUMO + 3 (33%) HOMO → LUMO + 3 (27%)
6a	1066.9	0.0148	HOMO-6 → LUMO (90%)
6b	821.7	0.2457	HOMO-2 → LUMO + 2 (16%) HOMO-2 → LUMO + 1 (15%)
	851.8	0.1634	HOMO-1 → LUMO + 1 (40%)
6c	785.3	0.1997	HOMO-2 → LUMO + 3 (30%)
	948.2	0.1683	HOMO-4 → LUMO (37%)
6d	766.47	0.2524	HOMO-1 → LUMO + 3 (23%)
	806.2	0.1836	HOMO-2 → LUMO + 1 (18%)
7	2365.2	0.0435	HOMO-1 → LUMO (61%)
	1467.8	0.0321	HOMO-4 → LUMO (91%)
8	2824.9	0.0449	HOMO → LUMO + 1 (39%) HOMO-1 → LUMO + 1 (25%)
	1699.6	0.0441	HOMO-4 → LUMO (74%)

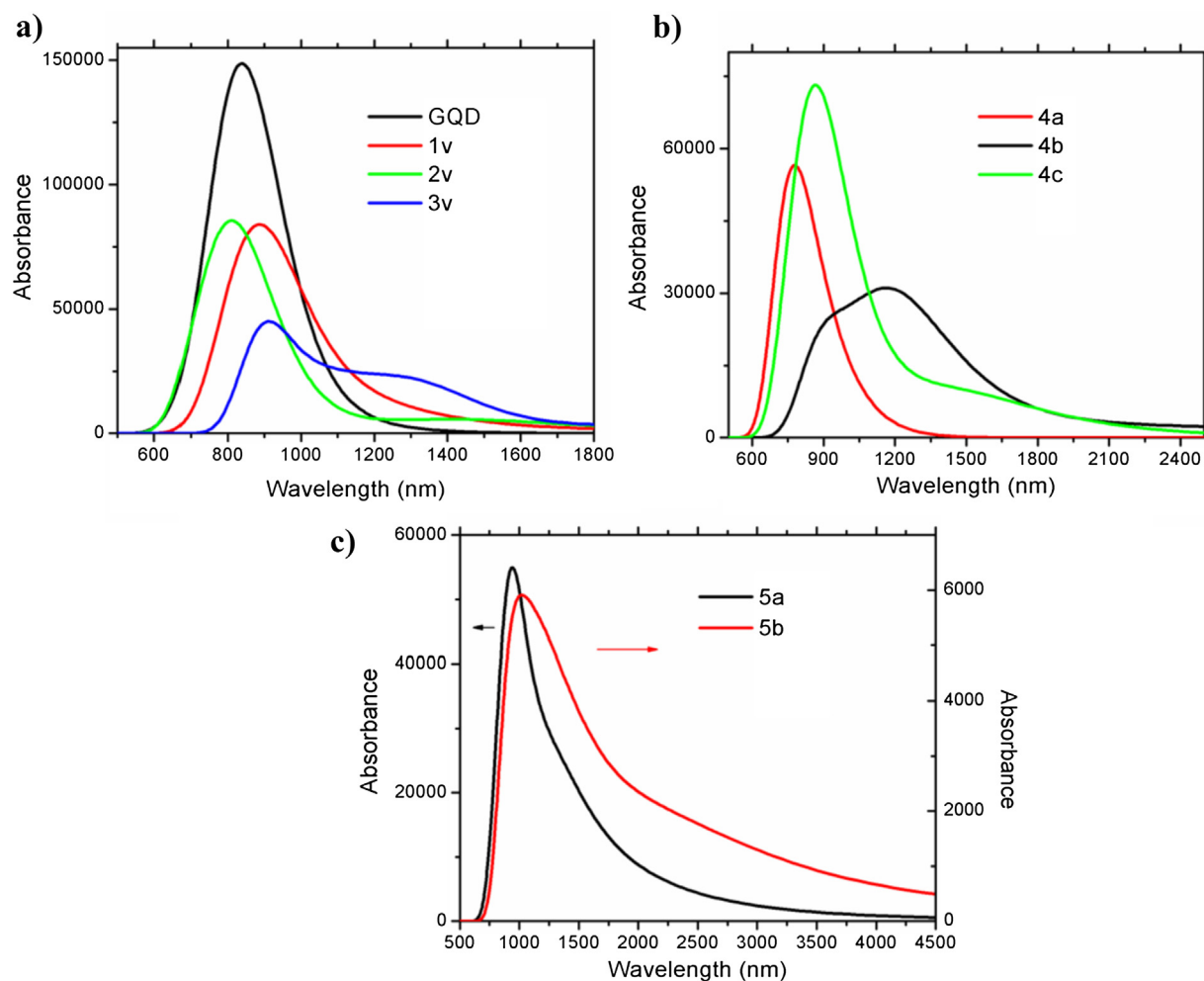


Fig. 8. Absorbance spectra for (a) non vacancy GQD, 1–3, (b) 4a, 4b, 4c and (c) 5a, 5b structures.

in Fig. 10, they have key roles in the main contribution transitions that are responsible for their spectra. As it can be seen from this figure, some structures such as 4a could develop promising properties for its applications in the design of solar cells [30]. In contrast to the non-vacancy system, in this case the HOMO level is below the energy level of ITO (indium tin oxide) ~ -4.7 eV [30]; which is represented as a blue horizontal line in Fig. 11. In addition, both the HOMO (~ -4.8 eV) and energy gap (~ 1.5 eV) values observed for 4a are close to those

observed for some thiophene-derived polymers; widely used as donor materials in organic solar cells [31]. Nonetheless, it is important to mention that the oscillation strength is lower than the observed for the non-vacancy system. However, the presence of multivacancies clearly modulates not only the electronic properties but the shape of the functionalized QDs leading to new insights which should be considered for their applications in solar cell devices.

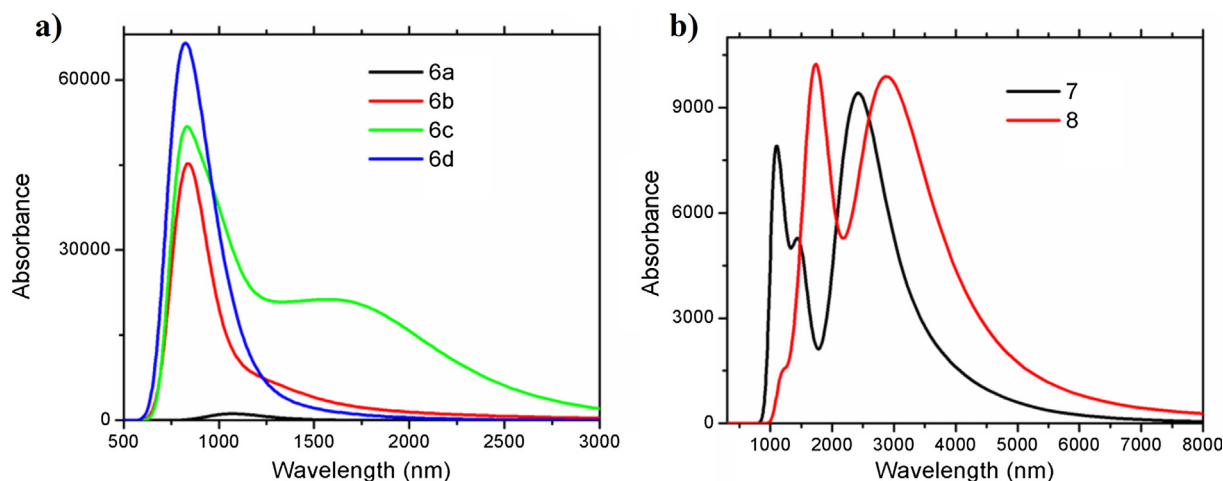


Fig. 9. Absorbance spectra for (a) 6a, 6b, 6c, 6d and (b) 7 and 8 structures.

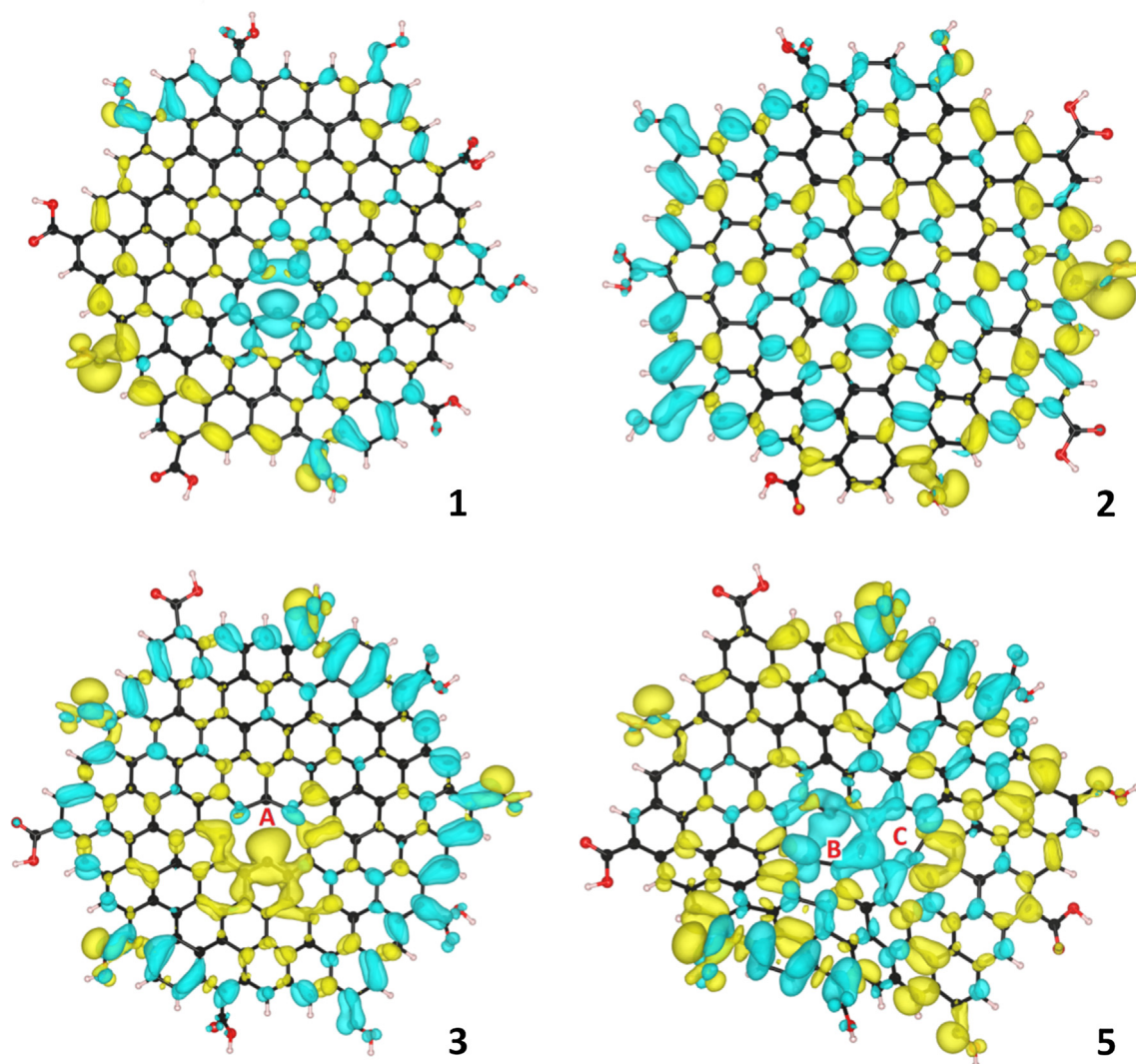


Fig. 10. Electronic density differences maps (EDDM) for 1, 2, 3 and 5a structures, where blue regions indicate a gain of electron density in a transition to the excited state and yellow regions indicate a loss of electron density in the transition to the excited state. The explanation for the labels A, B and C for the cycles is in text [32]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

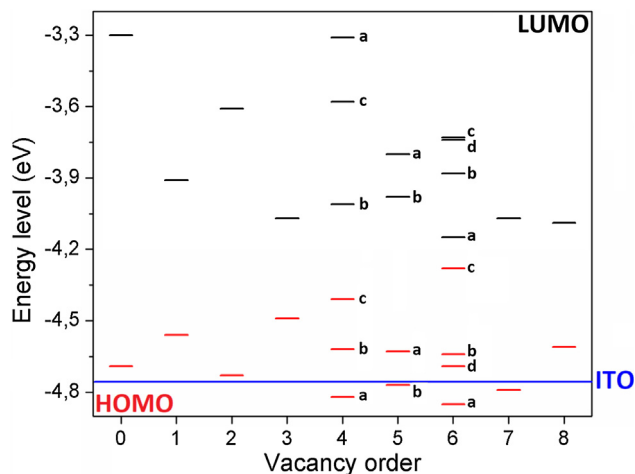


Fig. 11. HOMO and LUMO energy levels for all the multivacancy GQDs systems in this report. Blue line shows the HOMO energy level of ITO. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusions

A systematic study of the presence of vacancies with different configurations was performed for a GQD with formula $C_{160}H_{30}O_{15}$. These multivacancy systems are characterized for the occurrence of a curvature, mainly -but not exclusively- determined by the presence of pentagonal figures, or even square ones. Thus, the number of the pentagonal figures and their relative distance, along with their configuration, can be used to achieve an approximation of a curvature parameter, defined in this manuscript. The presence of higher order cycles -i.e. 7–12 membered ones-, some of them even detected experimentally [27,28], gives specific geometric features that prevent to find a general predictive model for the curvature, due to a contribution totally dependent on the particular case.

Although the trend of the formation energy in these systems follows the equivalent cases in graphene, an exception has been seen for the multivacancy GQDs systems created through the extraction of dendritic complementary figures. These cases are more unstable than the zigzag cases for the same vacancy order in GQDs, whilst they were more stable in graphene.

The band gap for these systems are in the infrared region and two anomalies were found for $N = 3$ and 5 in the zigzag series, that could be attributed to the presence of 10 and 9-membered rings.

The study here presented, where the characterization of the optical properties as a function of the vacancy order and configuration has been studied, could be important for potential applications in the design of solar cells.

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