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FULL PAPER

Evidence of benzenoid domains in nanographenes

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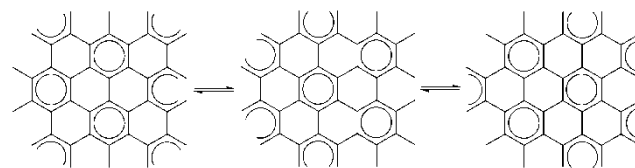
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Calculations based on density functional theory demonstrate the occurrence of local deformations of the perfect honeycomb lattice in nanographenes to form arrangements, with triangular symmetry, composed by six-membered ring patterns. The formation of these locally regular superstructures, which can be considered as benzenoid-like domains on the 2D graphene lattice, is ascribed to the gain in resonance energy deriving from aromaticity. The relationship between atomistic morphology of nanographenes and details of the relaxed structure is rationalized in terms of Clar's theory of the aromatic sextet and by extending concepts borrowed from valence bond theory to 2D carbon nanostructures. Namely, two regular arrangements can be evidenced, defined as Clar (fully benzenoid) and Kekulé domains, which correspond to two different regular bond patterns in sets of adjacent six-membered rings. Our findings are compatible with recent experiments and have potentially relevant consequences in the development of novel electronics devices based on graphene materials.

A Introduction

Low-dimensional nanostructured forms of graphene, as graphene quantum dots (GQDs)^{1,2} and graphene nanoribbons (GNRs),^{3,4} have recently attracted remarkable interest, which is related to their unique structural, optical and electrical properties.^{5–7} Indeed, the presence of terminations in nanographenes (NGs), with one or more finite dimensions in length domains in the order of the nanometer, gives rise to edge effects and quantum confinement. These effects, in turn, induce a deformation of the band structure of graphene and trigger the bandgap opening^{8,9} and can thus be exploited to realize nanostructured devices with tailored electronic properties.¹⁰ In this respect, experimental and theoretical work established the key role of edge terminations, usually constituted by zigzag or armchair edges or combinations thereof, in the definition of the properties of NGs.^{11–13} Nevertheless, several properties of NGs, including electronic structure, depend on the details of their morphology at the nanometer and atomistic scales.¹⁴ However, many aspects relating the structure of morphologically complex NGs and their electronic properties are still unclear.

Recent investigations demonstrated the possibility of interpreting the electronic structure of low-dimensional carbon nanostructures in terms of valence bond (VB) theory by extending classical organic chemistry concepts, such as Clar sextet theory,¹⁵ to carbon nanotubes (CNTs)^{16–19} and NGs.^{20–23} According to VB theory, the electronic structure of a planar sheet of graphene can be considered as the hybrid of three degenerate “fully benzenoid” VB forms. Each of the fully benzenoid resonance structure is formally constituted by a network of benzene-like (or benzenoid) rings, with localized π sextets, connected by single carbon-carbon bonds. Therefore, each of the



Scheme 1

three degenerate fully benzenoid representations of graphene is defined according to a superlattice of six carbon atoms, with vectors $(\sqrt{3} \times \sqrt{3})R30^\circ$ with respect to the lattice of pristine graphene, as shown in Scheme 1. Analogously, the VB representation of other finite or low-dimensional systems based on the graphene sheet (CNTs, NGs, etc.) can generally be considered as constituted by a network of six-membered benzenoid and non-benzenoid rings connected by single and/or double carbon-carbon bonds.¹⁶ The original formulation of Clar's theory is able to rationalize the significantly larger stability of systems constituted by a network of benzenoid rings only with respect to their non-benzenoid (i.e. less aromatic) counterparts in terms of the gain in energy associated to aromaticity.²⁴ The strong relationship between morphology and underlying VB representation has been supported by experimental and theoretical studies on polycyclic aromatic hydrocarbons (PAHs), which can be viewed as particular forms of hydrogen-terminated GQDs.^{25,26} Similar correlations between stability and tendency towards the formation of fully-benzenoid structures can also be expected in NGs, which can potentially undergo structural distortions with respect to the perfect hexagonal lattice of ideal graphene driven by the enhancement of their aromaticity. Nevertheless, deviations of the structural and electronic properties from those expected for an ideal system composed of a perfect (planar or rolled) hexagonal network of carbon atoms

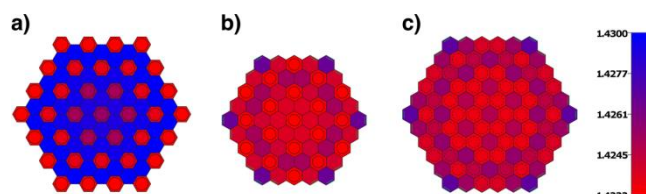


Fig. 1 VB representations of the optimized structures of a) A8-GQD, b) Z5-GQD and c) Z6-GQD. Six-membered rings are color-coded according to their MBL; values in the scale bar are in Å. Carbon-carbon bonds in green correspond to bond length shorter than 1.393 Å.

have recently been observed in CNTs²⁷ and NGs.²⁸ Consequently, in generic NGs the local relaxation of the hexagonal lattice to form a network of benzenoid rings could eventually lead to the formation of domain patterns and interfaces.

In this work, we show, by means of density functional theory (DFT) calculations, the occurrence of benzenoid domains in a variety of forms of NGs and relate the observed distortion to the extra stability associated to resonance energy. We base our conclusions on evidences provided by the analysis of both structural and electronic properties and compare our findings with the outcome of recent experiments. Our calculations indicate the formation of benzenoid patterns upon relaxation as a general feature of finite-size honeycomb-like arrangements of sp^2 carbon atoms and, as such, likely to occur in different forms of NGs, in analogy with Peierls distortion observed in metallic carbon nanostructures.²⁹ It must be pointed out that a direct link between molecular orbital (MO) calculations and the VB picture is generally not straightforward. However, a connection between these two approaches has already been demonstrated.³⁰ Indeed, properties derived from Kohn-Sham orbitals agree remarkably well with Clar analysis and with experimental data,²⁴ as for example demonstrated by investigations on the nucleus-independent chemical shift (NICS) of aromatic systems.^{31,32} To perform our analysis, we employed a large set of models of GQDs of different size, shape and edge terminations. Dangling bonds at the edge of NGs were saturated with hydrogen, to preserve the sp^2 hybridization of carbon atoms, similarly to previous work.^{20,21,33}

B Computational Details

Calculations were performed by applying the PBE³⁴ gradient-corrected approximation to DFT and using a basis set of double- ζ plus polarization quality for orbital expansion. Geometries of all models were optimized by relaxing all the nuclear degrees of freedom until convergence to a maximum force of 0.02 eV/Å on atoms. Geometries were analyzed by computing the mean bond length (MBL), defined as the mean value of the six C–C bond lengths in a given ring, for all six-membered rings in NGs, as done in previous work.^{22,27,35} Spin polarization was checked in all cases and subsequent calculations and analysis were performed on the most stable spin state. All calculations were performed with the Siesta program package.³⁶ To check our results, we also performed calibration calculations using the widely adopted B3LYP exchange-correlation functional and the G09 program package³⁷ (see ESI), leading essentially to similar conclusions.

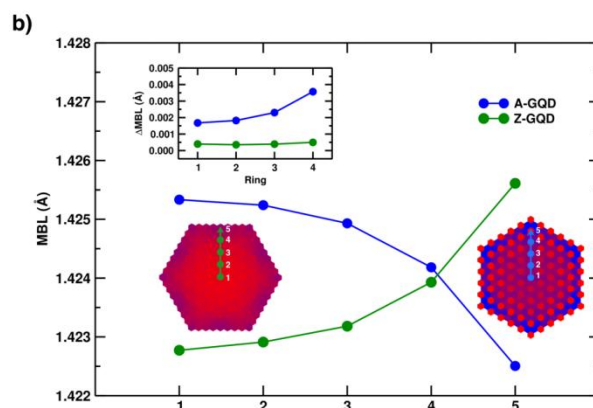
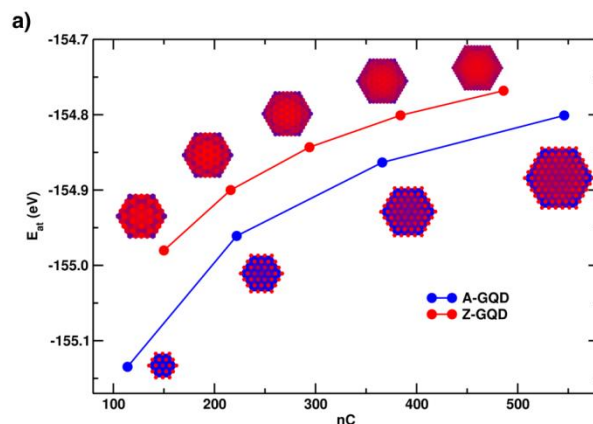


Fig. 2 a) Total electronic energy per carbon atom as a function of the total number of carbon atoms for symmetric models of A-GQDs (blue symbols) and Z-GQDs (red symbols). The energy per carbon atom of a GQD is computed as $E_{at} = (E_{NG} - n_H E_H) / n_C$, where E_{NG} is the total energy of the NG, n_H and n_C are the number of hydrogen and carbon atoms, respectively, and E_H is the energy of atomic hydrogen. b) MBL as a function of the distance from the GQD edge, for the A12-GQD (blue symbols) and the Z9-GQD (green symbols). Inset: Mean difference between the MBL of a ring and those of corresponding adjacent rings.

C Results and Discussion

As previously stated, the morphology of NGs has a strong impact on the resulting electronic properties³⁸ influencing in particular aromaticity.^{39,40} In turn, the aromaticity of a given NG can be related to the underlying VB representation. As a result, the morphology of a given NG, which depends on how the NG is formally cut from the infinite graphene sheet, and the nature of edge terminations determine the underlying VB representation. This latter accounts for the localization of benzenoid rings, single, and double bonds over the honeycomb lattice.²⁴ For example, an ideal fully-benzenoid GQD, i.e. with π electrons localized as π sextets only, can formally be obtained by cutting a portion of the infinite graphene sheet to generate a GQD with all-armchair edges (A-GQD). The optimized structure of a prototypical fully-benzenoid A-GQD, with 8 carbon atoms on each edge (A8-GQD), is depicted in Fig. 1a. In this and in the following figures, hexagons are colored according to the computed mean bond length (MBL), as defined by Dobado *et al.* in previous work on CNTs.^{27,35} The MBL allows to measure and

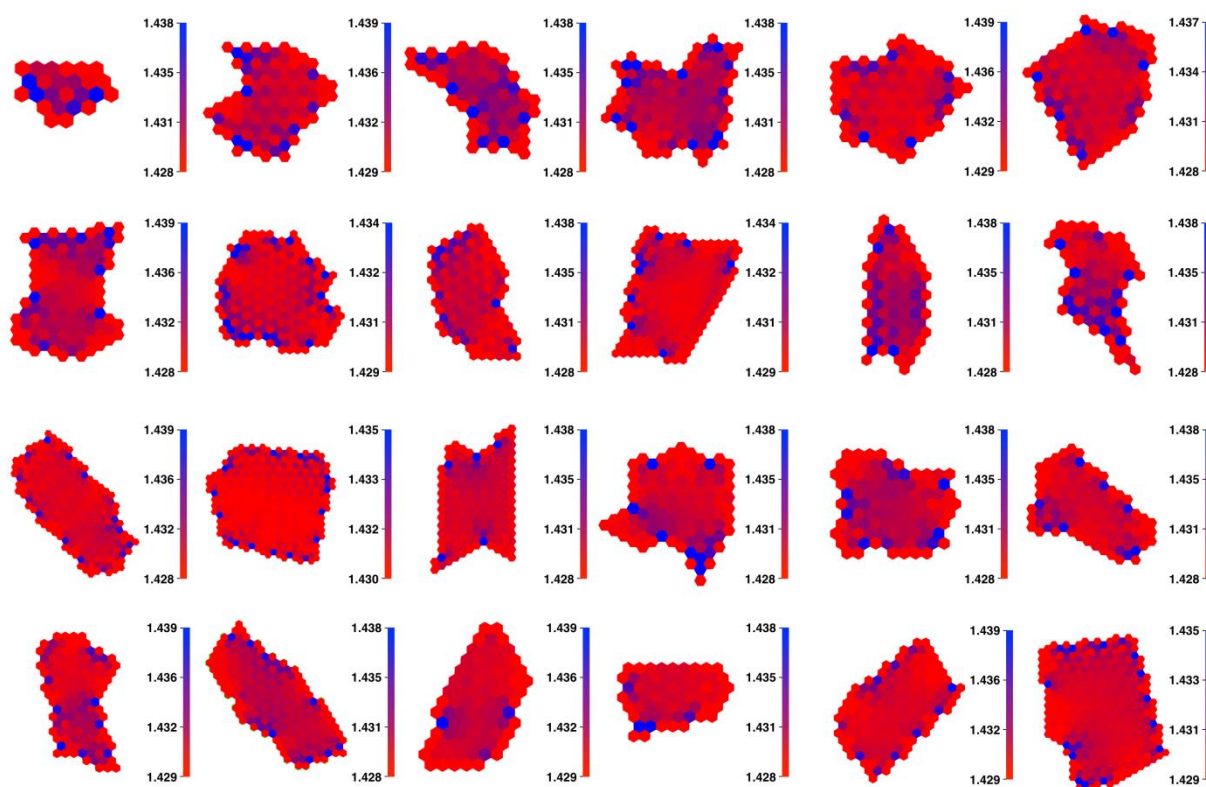


Fig. 3 Optimized geometries of the set of samples considered in this work. Structures are color-coded as in Fig. 1; values in the scale bar are in Å.

visualize the degree of localization of π sextets within the same ring, where C-C bonds are expected to be shorter than in rings with a lower localized density of π electrons.

Geometry relaxation of the A8-GQD in Fig. 1a leads to a sizeable (up to 4% for the C-C bond length) distortion of the pristine lattice of graphene, with a localization of benzenoid rings recovering the underlying VB pattern typical of Clar domains^{18,27} and distributed according to the superlattice shown in Scheme 1. Larger GQDs with the same symmetry undergo similar structural distortions, as suggested by Clar's theory (see Fig. ESI1a). However, the number of possible resonance structures with full or partial benzenoid character increases with the size of the GQD. Consequently, the energy split between the most stable (fully benzenoid) VB structure and higher energy (unrelaxed) forms is expected to decrease by increasing the size of the GQD. Moreover, relaxation into a structure corresponding to a network of localized benzenoid rings is also observed in generic A-GQDs with different shapes (see Fig. ESI1b), thus indicating a general validity of the above considerations. Conversely, the VB representation of GQDs with all-zigzag edges (Z-GQDs) is not fully benzenoid, with localized C-C double bonds in the most important resonance hybrids, as for example suggested by the DFT optimized structures of two Z-GQDs with 5 and 6 carbon atoms on each edge, shown in Fig. 1b and 1c, respectively.

Similarly to A-GQDs, the observed relaxation in Z-GQDs is qualitatively independent on the size and symmetry of the GQD (see Fig. ESI1c). Moreover, the VB patterning of symmetric Z-GQDs depends on the length of the edge, as is evident by comparing Fig. 1b with Fig 1c. However, the analysis of bond

lengths in the optimized structure indicates a clear Clar-like patterning also in models of Z-GQDs, consistently with the underlying VB representation, as shown in Fig. 1b. Therefore, in Z-GQDs resonance energy can drive the relaxation towards formation of localized benzenoid domains, despite the larger number of low-energy resonance hybrids with respect to fully benzenoid structures, dominated by a single (localized) resonance hybrid. Interestingly, depending on the GQD morphology, relaxation can also lead to localization of Kekulé domains^{18,20,27} (see Fig. 1c), which represent another modification of the graphene sheet with the same lattice of the structure in Scheme 1.

In agreement with the VB picture, the gain in resonance energy for fully benzenoid A-GQDs accounts for a higher stability with respect to Z-GQDs (see Fig. 2a), as previously observed in GNRs.^{20,39} Although the total energy per carbon atom is expected to converge, by increasing the size of the GQDs, to the limit value of graphene,⁴¹ the role of different morphology and bonding patterns on total resonance energy can still be observed in GQDs constituted of several hundreds of carbon atoms, thus corresponding to samples in the nanometer scale. Moreover, the MBL in inner rings of Z-GQDs is smaller of that in A-GQDs, as shown in Fig. 2b, thus suggesting a decoupling between localization and edge effects in large GQDs. Namely, the mean difference between the MBL of a ring and those of adjacent rings (see inset of Fig. 2b) exhibits a slight decrease in A-GQDs by increasing the distance from the edge, and is essentially constant in Z-GQDs, indicating the persistence of the Clar-like patterns described above. These structural details and, most importantly, localization properties of the electronic density are expected to

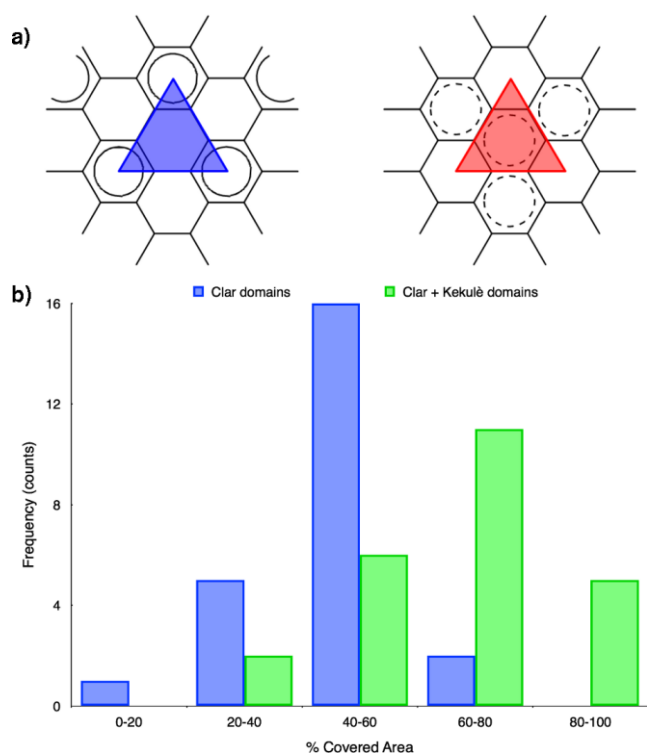


Fig. 4 a) Definition of Clar (left) and Kekulé (right) domains. b) Distribution of the 24 GQD samples in Fig. 3 according to the fraction of the surface area patterned by the domains in Fig. 4a. Blue bars: Clar domains; green bars: sum of Clar and Kekulé domains.

play a relevant role in the development of devices based on NGs.

Beside the limiting cases of the symmetric A-GQDs and Z-GQDs discussed above, real NGs exhibit a variety of morphologies and edge terminations, as shown in recent experiments.^{13,42} Yet, the relationships between edge effects, tendency toward the localization of π -sextets, lattice relaxations, and consequent occurrence of Clar and/or Kekulé domains and can also be applied to generic NGs. In particular, the energy lowering due to resonance can be expected to induce a local reorganization of the electronic structure in different regions of space of a given NG corresponding to benzenoid domains and interfaces thereof. To support this hypothesis, we optimized the structure of 24 different GQDs with randomly generated edges and shapes, and size ranging from about 2 to 6 nm for the longer axis, thus comparable to the size of GQDs investigated in recent experiments.⁴² The detail of the algorithm for generating the GQD models, is given as ESI, while the optimized geometries of the whole set of samples are shown in Fig. 3.

Visual inspection of the optimized geometries according to the color code described above reveals the occurrence of extended regions, in the GQDs considered, where ring sizes are distributed according to a Clar patterning, thus corresponding to benzenoid domains. To obtain a quantitative picture of this effect, we performed a statistical analysis of the optimized geometries for the set of GQDs under study. To this end, we defined a minimal Clar domain as constituted by four neighboring rings, with triangular symmetry, identified by three connected benzene-like units, as depicted in Fig. 4a (left). Similarly, we also defined a Kekulé domain, as shown in Fig. 4a (right). Then, different

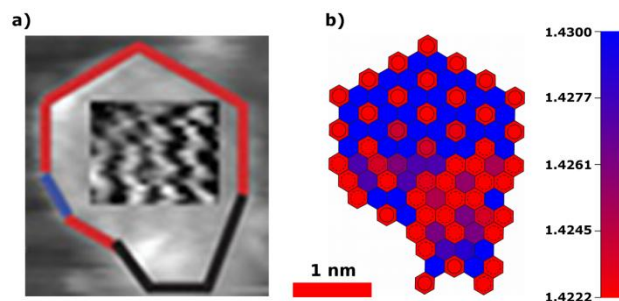


Fig. 5 a) STM topographic images and topographic derivative (inset) of a GQD taken from Ref.⁴² with edges assigned to armchair (red), zigzag (blue) and unassigned (black) terminations. Dark/bright contrast of the STM topographic derivative highlights the atomistically-resolved structure. b) optimized geometry and VB representation of a model of the same structure. Six-membered rings are color-coded according to their MBL; values in the scale bar are in Å. Adapted by permission from Macmillan Publishers Ltd: Nature Materials, copyright 2009.

regions of the GQDs were assigned to Clar or Kekulé domains by analyzing the occurrence of patterns in Fig. 4a on the basis of the optimized geometries. According to this definition, the extension of Clar domains is equal to 100% in the A-GQD of Fig. 1a and to 70% in the Z-GQD of Fig. 1b, due to the partial localization of π -sextets in this latter, as discussed above. Similarly, the structure of Z-GQD of Fig. 1c can be assigned to 26% of Clar domains and 74% of Kekulé domains.

Similarly, the occurrence of Clar and Kekulé structuring was also quantitatively evaluated for all 24 samples of Fig. 3 by computing the overall surface area of optimized geometries patterned by domains defined as in Fig. 4a. The samples considered were then classified upon the fraction of the total surface area patterned by Clar domains (blue bars in Fig. 4b). Moreover, the fraction of the surface area patterned by either Clar or Kekulé domains was also computed (green bars in Fig. 4b) to provide a measure of the overall occurrence of structured domains in the samples considered. Computed results for the set of 24 GQDs indicate a marked occurrence of benzenoid domains in most of the GQDs considered, with an average of around 46% of the rings arranged according to a Clar-like patterning (see blue bars in Fig. 4b). Moreover, if Kekulé domains are also taken into account, the average patterning of the GQDs increases to 68%, with most of the samples in the range 60%-80% (see green bars in Fig. 4b).

In addition, we performed calculations on a model of a GQDs reflecting the morphology, in terms of shape and edge terminations, of systems recently investigated by scanning tunneling microscopy (STM) by Ritter et al.,⁴² where a peculiar arrangement of the electronic density, with triangular symmetry, was observed. In particular, we made use of the structural information provided in Ref.⁴² concerning the size and the morphology (armchair or zigzag) of the edges to reproduce an accurate model of a typical GQD as observed in the experiment. The comparison between the STM structure of one of the GQDs analyzed in Ref.⁴² and the optimized geometry of the corresponding model is shown in Fig. 5. For the GQD in Fig. 5, the computed fraction of Clar and Kekulé patterning amounts to 82% of the total surface area, with a triangular motif consistent

with the symmetry of the electron density observed in other experiments⁴³ and compatible with the $(\sqrt{3} \times \sqrt{3})R30^\circ$ superlattice shown in Scheme 1.⁴⁴ Moreover, the sample analyzed in Fig. 5 exhibits distinct non-overlapping regions, which can be assigned to Clar and Kekulé domains, respectively, and suggests the possible formation of stable boundaries between large superstructures with local triangular symmetry.

Conclusions

In summary, theoretical calculations provide evidence of the formation of benzenoid-like domains in nanographenes as a result of the relaxation of the honeycomb lattice in finite-size systems. Calculations performed on hydrogen-terminated systems, to preserve the sp^2 hybridization of carbon atoms at the edges, indicate that the most stable bonding pattern corresponds to the formation of Clar (fully benzenoid) domains, where the π electron density is mostly localized in clusters of sextets. Depending on the local bonding situation, Kekulé patterning may also be observed. The occurrence of Clar and Kekulé patterning in generic GQDs is ascribed to the contribution to stability related to resonance energy and can be rationalized in terms of VB theory. The local structure of nanographenes can thus be described in terms of a superlattice with a six-membered ring in the unit cell. The precise knowledge about the localization properties of the electronic density is a key factor in the development of nanoelectronics devices and constitutes a crucial prerequisite for the engineering of novel nanomaterials for electronics based on graphene.

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Notes and references

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[†] Electronic Supplementary Information (ESI) available: Optimized geometries of A-GQDs and Z-GQDs samples. Description of the algorithm used to generate the GQDs samples of Fig. 3. Comparison between calculations performed with different exchange-correlation functionals. See DOI: 10.1039/b000000x/

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