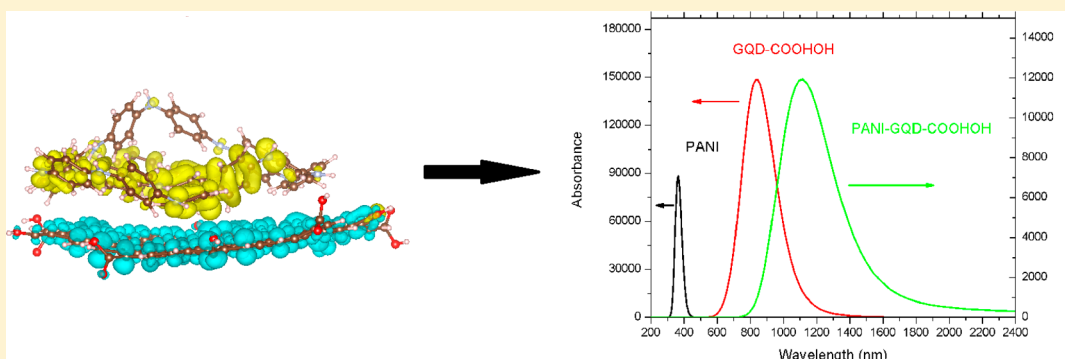


Electronic Structure of Edge-Modified Graphene Quantum Dots Interacting with Polyaniline: Vibrational and Optical Properties

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S Supporting Information



ABSTRACT: There are recent experimental reports on the preparation of edge-modified graphene quantum dots (GQDs) and its loading into conductive polymers for energy applications. Recently, we have studied the influence of the graphene quantum dots (GQDs) addition to polyaniline (PANI) conductive polymer in the electronic transport, finding important modifications in the structural and electrical properties respect to the pristine polymer. In this work, we present a mixed approach, based in first-principles molecular dynamics with time-dependent density functional calculations, for the description of the electronic dynamics, particularly for the determination of the optical properties. We found that edge modification of the GQDs favors the PANI/GQDs interaction, promoting very interesting electronic properties. Particularly, when hydroxyl chemical functional groups are present at the edges of the GQD a very good electron–hole separation during the photon excitation is obtained, demonstrating its potential use for optical applications in general and solar cells in particular.

1. INTRODUCTION

There is a recent interest in the preparation and characterization of conductive polymer-based devices for photo-response,^{1–3} sensing,⁴ and energy conversion⁵ applications. Polyaniline (PANI) is one of the most studied conductive polymer due to its easy preparation, low cost, and high conductivity.⁶ There are recent reports on the preparation and electrical transport properties on PANI-based nanocomposites, including the additions of different materials, particularly graphene quantum dots (GQDs).^{2,3} The literature shows very interesting works that use first-principles methods to understand the mechanism of growth of carbon nanostructures, see, for example, Goyenola et al.⁷ However, there are very few theoretical insights regarding the edge modification chemical nature of these GQDs and its electronic interactions with conductive polymers. Our research group contributed experimentally for the understanding of the correlations between the chemical structure and its electronic properties,² although it was only for the case of aggregates of small percentage of GQD to PANI. The interplay between donor–acceptor properties are crucial, not only for the electrical transport, but also for the optical response that could be of interest for solar cells.⁸ Many of these properties are directly affected for the electronic structure of the systems, thus it is very relevant to perform

quantum-chemical simulations in order to get insight on these properties.

However, due to the complexity and the considerable number of atoms involved in a “first-principles” calculations, it is necessary to apply mixed methodologies. That is the reason why in literature very few reports on the topic are found, considering the modeling but utilizing small size PANI monomers,⁹ or even performing periodic boundary calculations with small unit cells that limit the potential geometry optimization of the corresponding polymers.^{10–12}

Here we present a very first approximation for the quantum chemical modeling of nanocomposite systems, considering a moderate number of atoms to describe the interaction between PANI-GQDs nanocomposites. Our methodology involves first a density functional theory (DFT) molecular dynamics (MD) simulation, followed by a time-dependent density functional theory (TD-DFT) calculation, which is necessary to obtain an accurate description of excited states for a better description of vertical transitions. This last procedure allows us to get right optical and electronic structure description of the system.

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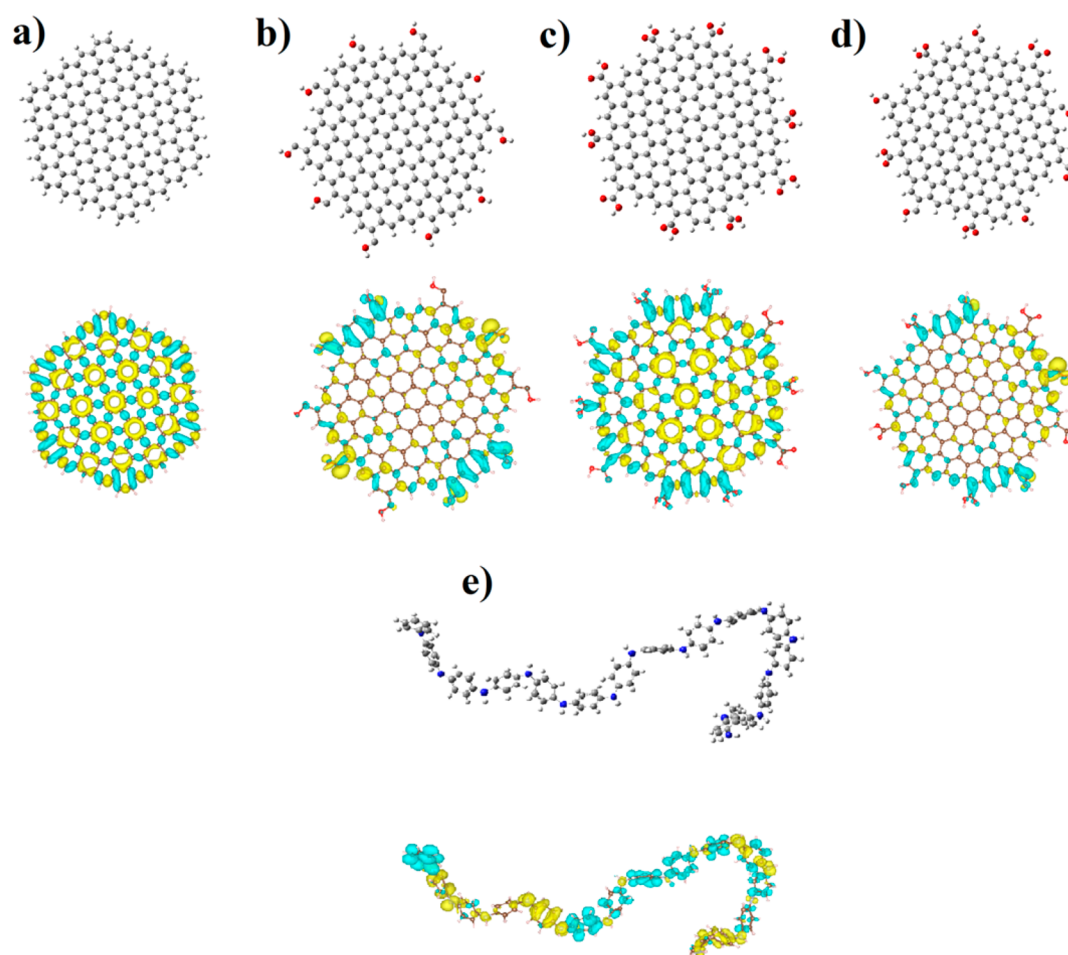


Figure 1. Structure and geometry for PANI-X with (a) X = H, (b) X = OH, (c) X = COOH, (d) X = COOHOOH, and (e) PANI. In the lower panel, we present the electronic density differences maps (EDDM) for the most intense optical transition. Note: Yellow regions indicate a loss of electron density in the transition to the excited state and blue regions indicate a gain of electron density in a transition to the excited state.

2. METHODS

As pointed out in the early section, our objective is to perform precisely first-principles calculations involving a considerable number of atoms. This task is limited by its computational cost but it can be addressed by combining molecular dynamics simulations, followed by well suited quantum-chemical calculations.

We considered four types of edge chemical functionalization named as GQD-X, where X = H, OH, COOH, and COOHOOH, which correspond to the following empirical formulas: $C_{150}H_{30}$, $C_{160}H_{30}O_{10}$, $C_{160}H_{30}O_{20}$, and $C_{160}H_{30}O_{15}$, respectively. These sizes of the molecules have been demonstrated as adequate for describing graphene or graphene oxide successfully from the vibrational point of view.¹³ In the case of the PANI polymer, we considered the emeraldine salt $[(C_6H_4NH)_2(C_6H_4N)]_n$ with $n = 7$, see Figure 1.

In order to get reasonably good starting geometries we perform DFT^{14,15} utilizing Gaussian 09,¹⁶ selecting the B3LYP^{17–20} xc-potential at the 6-31g(d) level of theory. Then, vibrational analysis is performed in order to confirm the stability and local minima in all the starting compounds.

For the modeling of the polymeric PANI/GQDs nano-composite, we performed molecular dynamics simulations, in the framework of DFT utilizing the SIESTA^{21,22} code. SIESTA adopts a linear combination of numerical atomic orbitals. We utilized double- ζ basis sets with polarization orbitals (DZP) for

all the atoms. We choose the van der Waals (vdW)-DF xc-potential as implemented by Dion et al.²³ within the LMKLL reparametrization of Lee et al.²⁴ We selected a mesh cutoff of MC = 200 Ry that ensures a dense grid for charge density of the system. With the aim to describe an isolated system, we constructed a unit cell sufficiently large for avoiding interaction among periodic images, thus choosing only the Γ -point for the Brillouin-zone sampling. After setting up the SIESTA simulation, we proceeded with the molecular dynamics simulation, selecting a NVT ensemble with a $T = 300$ K, and time step of 1 fs and a total time of 2 ns. The Nosé–Hoover thermostat was employed in this setup. This procedure allows us to map all the configurational space and thus provide an accurate description of this polymeric system.

Finally, we proceed with time-dependent DFT (TD-DFT)^{25,26} calculations, utilizing the same conditions for the Gaussian09 set up, selecting the first 20 singlet–singlet excitations for optical study. With this procedure, we will report on the energy interactions between GQD and PANI, and describe its potential use for optical applications.

3. RESULTS

3.1. Geometry Optimization and Vibrational Properties. As mentioned before, the basis of 150 carbon atoms for describing the graphene-like core in all the molecules have been demonstrated as adequate for the study of its vibrational

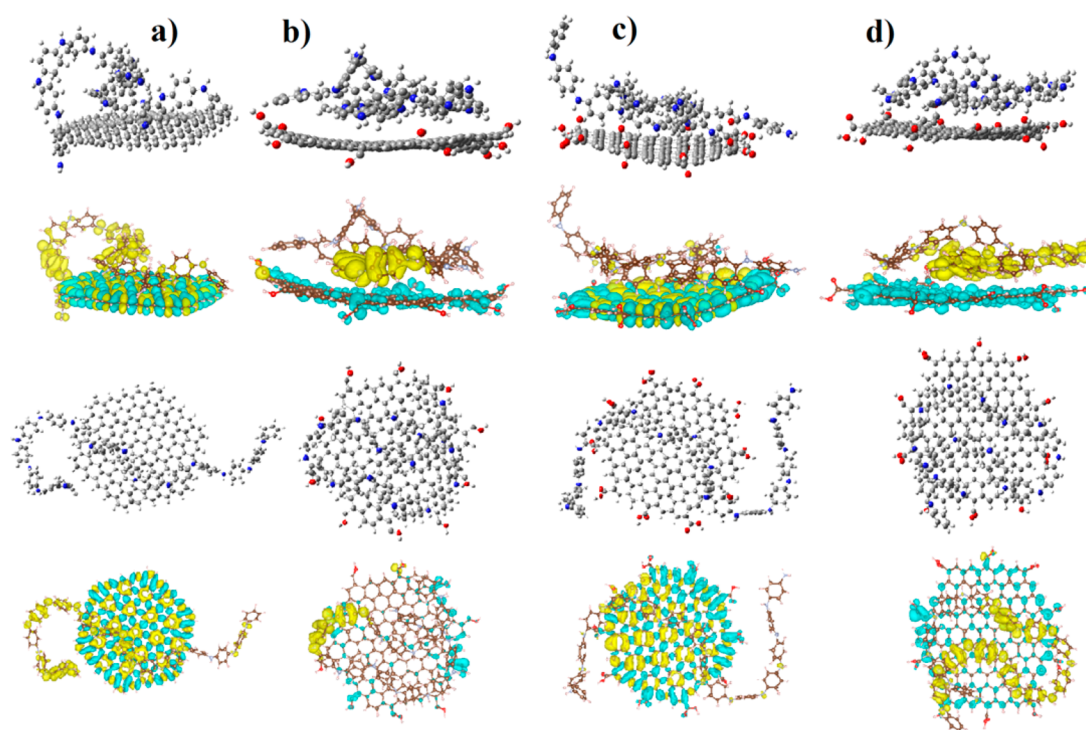


Figure 2. (Top rows) structure; (bottom rows) electronic density differences maps (EDDM) depicting the most relevant optical transitions for PANI-GQD-X with (a) X = H, (b) X = OH, (c) X = COOH, and (d) X = COOH OH. Note: Yellow regions indicate a loss of electron density in the transition to the excited state and blue regions indicate a gain of electron density in a transition to the excited state.

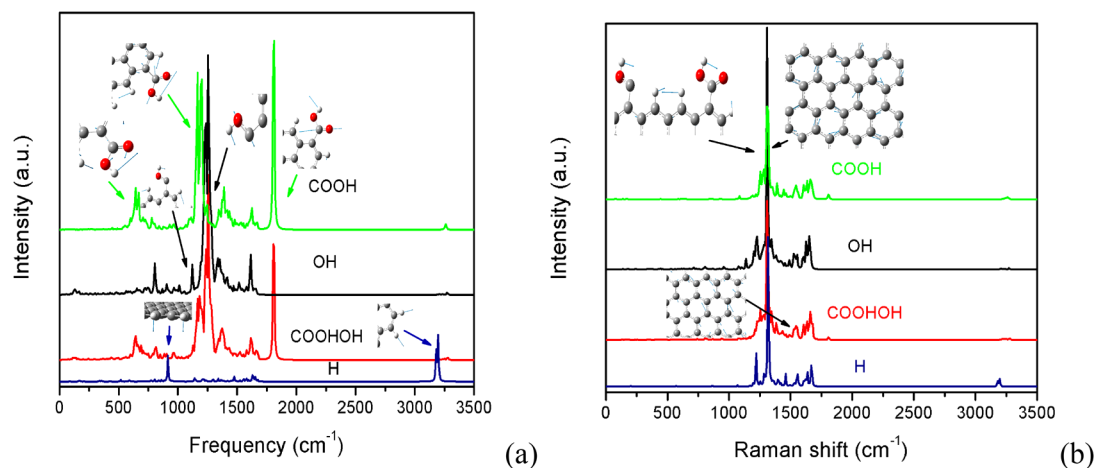


Figure 3. (a) IR spectra for GQD-X with X = H, COOH OH, OH, and COOH and (b) Raman spectra for GQD-X, with X = H, COOH OH, OH, and COOH.

properties.¹³ Anyway, the direct interpretation of the vibrational modes seems to be complex. In one hand, this is due to large number of atoms and thus the large number of degrees of freedom involved in the system. On the other hand, the chemical substitution breaks the symmetry and the degeneracy of modes, giving places to broad bands in the IR and Raman spectra too.

The first step involves the geometrical optimization of the four oxidized GQDs; the final geometries are presented in Figures 1 and 2. As mentioned before, we performed edge chemical doping, because edges show better formation energies²⁷ due to their higher chemical reactivity when compared to “bulk” atoms. In order to confirm the local minima of the obtained geometries, after performing the full

DFT geometrical optimization for the four structures we performed vibrational analysis including infrared (IR) and Raman spectra, see Figure 3. In all cases, the graphene plane remains flat with the most important structural changes localized at the edges.

In all the cases, we obtain all real frequencies and the spectra provides the main features for an easy identification of the different chemical functional groups.

When the Raman spectra are analyzed, there are no major differences between the different GQDs, see Figure 3. This is a consequence to the size of the GQDs, where the effect of the edge doping seems to be diluted and the differences becomes reduced. All the Raman spectra present the most intense peaks located at $1310 \pm 10 \text{ cm}^{-1}$, corresponding to the graphene-like

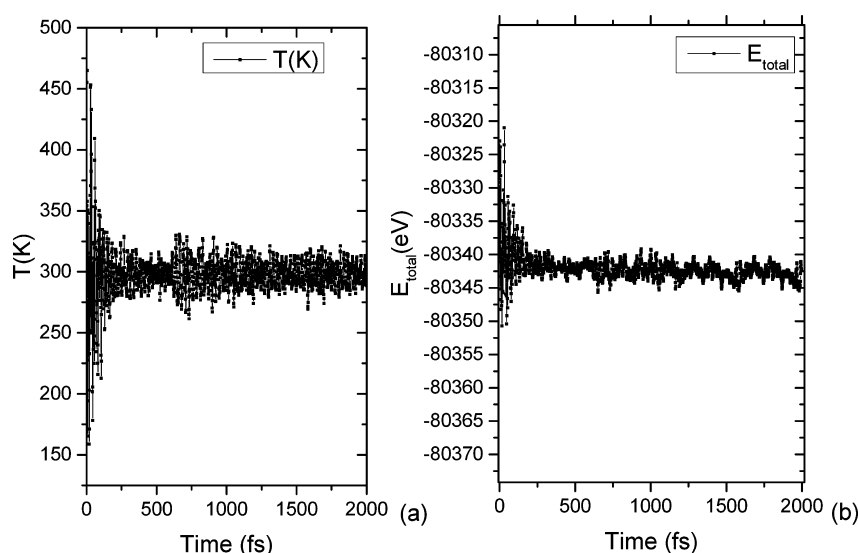


Figure 4. (a) Temperature and (b) total energy (E_{total}) evolution during the molecular dynamics simulation for PANI/GQD-H.

Table 1. Wavelength, Oscillation Strength, and Major Contribution for PANI-H, GQD-H, and PANI-GQD-H

	wavelength (nm)	oscillation strength	major contribution
PANI-H	358.2	0.4669	HOMO-2→LUMO+5 (25%) HOMO-3→LUMO+4 (18%)
	360.0	0.391	HOMO→LUMO+8 (29%)
GQD-H	748.1	1.2469	HOMO-1→LUMO (47%) HOMO→LUMO+1 (47%)
	749.9	1.2429	HOMO-1→LUMO+1 (49%) HOMO→LUMO (45%)
PANI-GQD-H	742.3	1.3218	HOMO-5→LUMO (46%) HOMO-2→LUMO+1 (44%)
	730.4	0.9398	HOMO-5→LUMO+1 (72%)

breathing band, ascribed to the stretching $\nu(\text{C}-\text{C})$, usually labeled as the graphene's G-band. In the case of bending modes of X-H, minor peaks can be observed at both sides of the main peak in the range of ~ 1200 – 1700 cm^{-1} . The peaks close to $\sim 1200\text{ cm}^{-1}$ correspond to $\delta(\text{C}-\text{H})$ bending modes. Then, the peaks close to $\sim 1700\text{ cm}^{-1}$ correspond to stretching plus bending $\nu(\text{C}-\text{C}) + \delta(\text{C}-\text{H})$ modes, mainly located at edge positions in this case. In the region of ~ 3150 – 3300 cm^{-1} , the stretching $\nu(\text{C}-\text{H})$ modes are identified. When considering the others GQDs, the contribution of -OH and -COOH functional groups are observed. As mentioned before, the bands in the Raman spectra changes slightly due to the presence of these groups and the symmetry breaking. In particular, the signals coming from the -COOH functional groups appeared as very weak in the region of $\sim 1800\text{ cm}^{-1}$, corresponding to the stretching $\nu(\text{C}=\text{O})$ mode. In the region of ~ 3650 – 3710 cm^{-1} , the stretching $\nu(\text{O}-\text{H})$ modes appeared for X = OH, COOH, and COOH.

When the IR spectra are analyzed, the situation changes due to the nature of the IR's selection rule, and the differences between all the GQDs are more evident. Figure 3 include the sketches of the most relevant vibrational modes of the IR spectrum. It is evident the contribution from the stretching $\nu(\text{C}=\text{O})$ mode of the -COOH groups. The contribution of the bending $\delta(\text{O}-\text{H})$ modes are observed in the region of $\sim 650\text{ cm}^{-1}$, contribution to the broadening of the whole vibrational spectra, as mentioned before.

Even though the vibrational differences are not so significant for a straight identification, the presence of characteristic bands, coming from the -COOH and -OH chemical functional groups, are possible to be identified. These characteristics will

become very different when addressing the optical properties, see further.

3.2. MD Simulations. The MD simulations demonstrate the good affinity between PANI and all the studied GQDs. An important distortion of the graphene plane is observed with an interesting interaction with the PANI polymer, in particular with the central region of the GQDs (see Figure 2). On this basis, we can state that there is a good affinity between both systems, justifying the study of its electronic structure, in particular describing the optical properties. For reference, we present in Figure 4 the total energy and temperature evolution during the MD simulation in SIESTA, demonstrating final stabilization of the system PANI/GQD-H.

In order to study the interaction between PANI and GQD-X system we calculated the interaction energy (E_{int}) according to $E_{\text{int}} = E_{\text{PANI/GQD-X}} - E_{\text{PANI}} - E_{\text{GQD-X}}$, where $E_{\text{PANI/GQD-X}}$, E_{PANI} and $E_{\text{GQD-X}}$ corresponds to the corrected total energy of PANI/GQD-X system, isolated PANI, and isolated GQD-X, respectively. Because of the localized nature of the utilized basis set, a "basis set superposition error" (BSSE), was incorporated by the implementation of total energy corrections, utilizing a floating basis set denominated as "ghost atoms" in the SIESTA code. The interaction energies correspond to -0.21, -2.66, -5.11, and -5.92 eV for X = H, OH, COOH, and COOH, respectively. There is not a clear tendency on the interactions energies, but what is clear is the necessity of the presence of oxidizing groups for the enhancement of the interaction between PANI and modified GQD.

3.3. Optical Properties. In order to study the optical properties of the PANI/GQD composites, we performed TDDFT calculations, describing the first 20 singlet-singlet transitions. We started this task, modeling the isolated GQDs

Table 2. Wavelength, Oscillation Strength, and Major Contribution for PANI–OH, GQD–OH, and PANI–GQD–OH

	wavelength (nm)	oscillation strength	major contribution
PANI–OH	371.9	0.1111	HOMO–2→LUMO+1 (78%)
	383.7	0.1046	HOMO→LUMO+3 (42%) HOMO–1→LUMO+3 (34%)
GQD–OH	921.8	0.834	HOMO–1→LUMO+1 (60%)
	910.8	0.4548	HOMO→LUMO+1 (28%)
PANI–GQD–OH	1375.2	0.054	HOMO–4→LUMO (55%)
	1517.0	0.0284	HOMO–8→LUMO (30%)

Table 3. Wavelength, Oscillation Strength, and Major Contribution for PANI–COOH, GQD–COOH, and PANI–GQD–COOH

	wavelength (nm)	oscillation strength	major contribution
PANI–COOH	372.2	0.7049	HOMO–1→LUMO+1 (73%)
	350.9	0.3953	HOMO–1→LUMO+6 (38%)
GQD–COOH	773.2	1.2795	HOMO–1→LUMO (37%) HOMO→LUMO+1 (35%)
	772.0	1.232	HOMO–1→LUMO+1 (45%) HOMO→LUMO (26%)
PANI–GQD–COOH	915.4	0.062	HOMO–5→LUMO (53%)

Table 4. Wavelength, Oscillation Strength, and Major Contribution for PANI–COOH–OH, GQD–COOH–OH, and PANI–GQD–COOH–OH

	wavelength (nm)	oscillation strength	major contribution
PANI–COOH–OH	364.2	0.3445	HOMO→LUMO+7 (33%)
	378.6	0.2525	HOMO→LUMO+6 (37%) HOMO→LUMO+7 (21%)
GQD–COOH–OH	853.6	0.925	HOMO–1→LUMO+1 (58%) HOMO→LUMO (30%)
	815.6	0.6124	HOMO–3→LUMO (27%) HOMO–1→LUMO (24%)
PANI–GQD–COOH–OH	1107.1	0.1225	HOMO–7→LUMO (38%) HOMO–5→LUMO (22%)

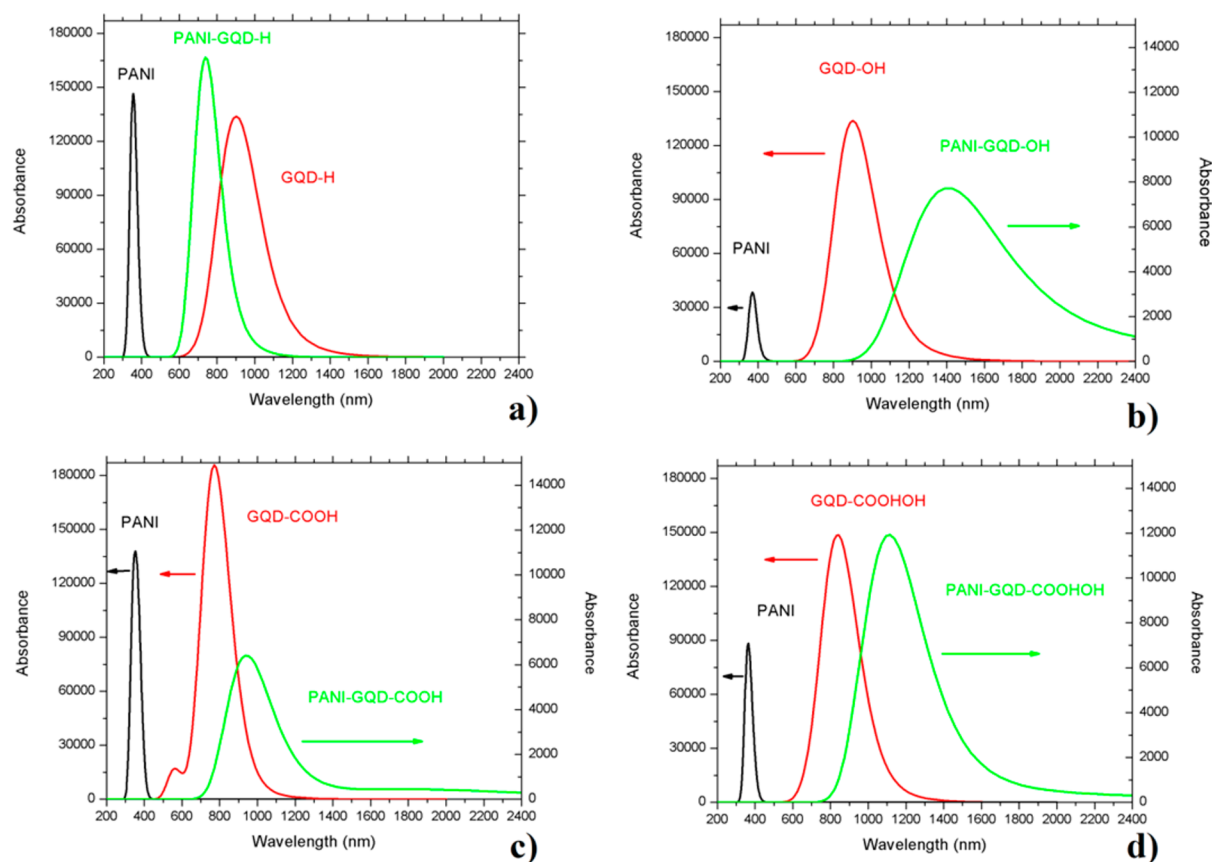


Figure 5. UV-vis spectra for (a) PANI, GQD–H, and PANI–GQD–H; (b) PANI, GQD–OH and PANI–GQD–OH; (c) PANI, GQD–COOH and PANI–GQD–COOH; and (d) PANI, GQD–COOH–OH and PANI–GQD–COOH–OH.

and PANI. Figure 2 presents the electronic density differences maps (EDDM) for the most intense optical transition, describing the gain and loss in the electron density as a consequence of the optical transition. Because of the organic chemical nature of the systems, all the transitions can be described as $\pi^* \rightarrow \pi^*$ for the GQDs and PANI. Tables 1, 2, 3, and 4 and Figure 5 collect all the relevant information for the optical properties of the system.

PANI. In the case of isolated PANI, we calculated the optical properties for this polymer in the final conformation for the four PANI/GQDs geometries. The differences in the structural conformations induce changes in the oscillation strength, but there are no relevant changes in the corresponding wavelength. For example, in the case of PANI-H the main electronic transitions are located at 358.2 and 360 nm with the most relevant contribution coming from HOMO-2 $\rightarrow$ LUMO+5 and HOMO $\rightarrow$ LUMO+8, leading to an oscillation strength of 0.467 and 0.391 respectively. In the case of PANI-OH, the main transitions are located at 371.8 and 383.7 nm with the main contributions of HOMO-2 $\rightarrow$ LUMO+1 and HOMO $\rightarrow$ LUMO+3, and the oscillation strength is reduced to 0.111 and 0.105 respectively. For PANI-COOH, the situation changes: the transitions are located at 350.9 and 372.2 nm with the main contribution from HOMO-1 $\rightarrow$ LUMO+6 and HOMO-1 $\rightarrow$ LUMO+1 but in this case the oscillation strength increased up to 0.3952 and 0.7049. Finally, for PANI-COOHOH, the main transitions are located at 364.2 and 378.6 nm, corresponding to the following main contributions, HOMO $\rightarrow$ LUMO+7 and HOMO $\rightarrow$ LUMO+6, with an oscillation strength corresponding to 0.344 and 0.253, respectively. As it can be observed, the main transition is always located in a limited range of 350 to 379 nm but with important changes in the oscillation strength that strongly depends on the chain conformation. In particular, when polymer chain becomes linear the oscillation strength increases.

GQDs. Here we proceed with an analogous treatment of the electronic structure of the isolated GQDs in their modified conformations when interacting with PANI. Here again, the most relevant optical transitions can be understood as $\pi^* \rightarrow \pi^*$ in general with an important role of the states coming from the central region of the GQD, that could be seen as a graphene-like region. The presence of different chemical substitutes, X = H, OH, COOH, and COOHOH, clearly changes the pure graphene electronic structure. In the case of GQD-H, the situation is the closest to the ideal graphene system with clear $\pi^* \rightarrow \pi^*$ transitions, highly delocalized in the core of the graphene sheet. The main transitions are located at 748.1 and 749.9 nm, described as HOMO-1 $\rightarrow$ LUMO/LUMO+1 and HOMO-1 $\rightarrow$ LUMO+1 with oscillation strength 1.247 and 1.243, respectively.

The situation changes for GQD-OH, not only due to the conformational changes of the central graphene region but mainly because of the change given by the breakage of symmetry introduced by edge doping, see Figure 1. Here, an important contribution to the frontier orbitals is observed with states coming from the edges of the structure. That is the reason why the main transitions now are more separated, located at 910.8 and 921.8 nm in comparison to other cases. The main transitions correspond to HOMO $\rightarrow$ LUMO+1 and HOMO-1 $\rightarrow$ LUMO+1 with oscillation strength 0.455 and 0.834, respectively.

In the case of GQD-COOH, the electronic π -states delocalization in the core of the graphene region is slightly

modified, presenting important similarities to GQD-H in difference to GQD-OH, see Figure 1. Now the main transitions are close located at 772.0 and 773.2 nm, corresponding to HOMO-1 $\rightarrow$ LUMO+1 and HOMO-1 $\rightarrow$ LUMO with oscillation strength of 1.232 and 1.280, respectively.

Finally, we discuss the GQD-COOHOH system, which due to the presence OH groups shows a situation similar to GQD-OH, see Figure 1. The main transitions are located at 815.6 and 853.6 nm with the main contributions of HOMO-3 $\rightarrow$ LUMO and HOMO-1 $\rightarrow$ LUMO+1 with oscillation strength 0.612 and 0.925, respectively.

In general, GQD-H and GQD-COOH present the main absorption peaks in a shorter range in wavelength and with stronger oscillation strength in comparison to GQD-OH and GQD-COOHOH. These differences arise from the nature of the frontier orbital due to the edge doping.

PANI/GQDs. When considering the PANI/GQD nanocomposite, the interaction induces important changes in the geometry, see Figure 2 and the corresponding electronic structure. As it was mentioned before, the geometrical structure and the corresponding binding energy indicates that GQD/PANI interaction is important.

In the case of PANI/GQD-H, there exists a blue shift in the absorption band in comparison to GQD-H with transitions located at 730.4 and 742.3 nm, described as HOMO-5 $\rightarrow$ LUMO+1 and HOMO-5 $\rightarrow$ LUMO with oscillation strength 0.940 and 1.322, respectively. With a closer inspection of the transitions, it could be understood as a PANI $\rightarrow$ GQD-H electronic transition, as observed in Figure 2. Nevertheless, there are some internal $\pi^* \rightarrow \pi^*$ from the GQD-H that decrease the degree of charge separation in the excitation process. Here, it is important to mention that when comparing to pure PANI and GQDs, the oscillation strength and thus the optical absorption is drastically reduced for the nanocomposite, but this is just for comparison purposes with the corresponding isolated systems.

When going to the PANI/GQD-OH case, we observe again a red shift of the absorption band in comparison to GQD-OH. The transitions are located at 1375.2 and 1517.0 nm, described as HOMO-4 $\rightarrow$ LUMO and HOMO-8 and LUMO, with oscillation strengths 0.054 and 0.0284, respectively. When analyzing the topography of the electronic transition, it is observed a clear $\pi^* \rightarrow \pi^*$ excitation from PANI to GQD-OH, thus constituting a very good charge separation during the transition.

In the case of PANI/GQD-COOH, the optical band exhibits a red shift when compared to GQD-COOH. The main transition corresponds to 915.4 nm, mainly represented as HOMO-5 $\rightarrow$ LUMO, with an oscillation strength of 0.062. In difference to PANI/GQD-H and PANI/GQD-OH, the excitation for PANI/GQD-COOH can be ascribed as a pure internal $\pi^* \rightarrow \pi^*$ transition in the core of GQD-COOH.

For PANI/GQD-COOHOH, there exists a red shift in the absorption band, when compared to GQD-COOHOH. The transitions are located 1107.1 nm, described as HOMO-7 $\rightarrow$ LUMO with oscillation strength of 0.123. When analyzing the topography of the excitation process, it is observed again a clear $\pi^* \rightarrow \pi^*$ excitation from PANI to GQD-COOHOH, similarly to PANI/GQD-OH, thus constituting a very good charge separation during the transition.

Finally, an important and interesting aspect is the study of the dependence of electronic properties as a function of the

concentration of GQD–X on PANI. But this constitutes with our methodology, an important computational demand. In the Supporting Information, we present the results for PANI/GQD–X (X = COOH) for ratios 2:1 and 3:1. What is observed is that the presence of more PANI chains generates a red shift of the $\pi^* \rightarrow \pi^*$ transitions when compared to the 1:1 ratio, thus contributing to the near-infrared region of the optical spectra. It is clear that the concentration effect plays a role, but what is still valid for all the studied systems is that the transitions with better oscillation strength involves $\pi^* \rightarrow \pi^*$ from PANI to GQD–X.

4. CONCLUSIONS

We have presented a mixed methodology utilizing MD-DFT simulations followed by very accurate TD-DFT calculations. We demonstrated that the electronic interaction between PANI polymer and GQDs is enhanced when oxidizing groups are incorporated in the GQD, which further introduces structural asymmetries, which is very relevant for the optical properties. In particular, the presence of OH groups at the edges of the GQD–OH and GQD–COOH reduces the symmetry of the electronic topography, favoring the charge separation upon an optical excitation, thus constituting a very promising system for optical applications in general and organic solar cells in particular. The main conclusion of the work establishes the potential use of nanocomposites PANI/GQDs for the tuning of the optical applications.

■ ASSOCIATED CONTENT

Supporting Information

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Additional information, tables, and figures (PDF)

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Notes

The authors declare no competing financial interest.

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