Electronic Supplementary Information #1 for

**Insights into the origin of the excited transitions in graphene quantum dots interacted with heavy metals in different media**

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1. **Pristine GQDs: solvent effect**

In principle, knowledge about the stability of the GQDs can help to prepare the GQD solution electrolyte, providing a desired sensitivity/selectivity to HM adsorbates. Here we compare the cohesive energies of zigzag- and armchair-edged GQDs immersed in different dielectric media. Calculated results are given in Table S1. For all dielectric media, ZZ-GQDs are more stable than AC-GQDs. In particular, cohesive energy of ZZ-GQDs is ~0.26 eV·atom-1 greater than AC-GQDs. This difference is due to the different regularity and symmetry of the GQDs boundaries. In addition, our model implies an enhanced hydrogenation of the edges in the case of the AC-GQDs and, as a consequence, a lower energy barrier to be overcome before bonding breaking occurs. The calculated cohesive energy is in good agreement with previously reported value of the cohesive energy of carbon in graphene, 7.4 eV per C atom.1 It should be mentioned that this energy refers to carbon atoms belonging to inner hexagonal rings, while the carbon species at the edges are expected to be less strongly bound. As one can see in Table 1, an increase in the solvent dielectric constant shows small effect on the cohesive energy (decrease only by ~50 meV), indicating a lowering of the stability of the GQDs. It is also evidenced by the changes in the electrophilicity index. This parameter gives an important information about the effect of the dielectric medium on the GQD stability. Increase in this index with increasing the dielectric permittivity means that the GQDs immersed in more polar solvents are less stable and more reactive.2,3

Changes in the cohesive energy are accompanied with changes in the solubility of GQDs (See Table 1). The calculated solvation energies, presented in Table S1, are negative in all cases. For both zigzag-edged and armchair-edged GQDs, the solvation energy is increased with increasing the solvent dielectric constant, reaching the maximum value for water. Furthermore, the solubility of GQDs in organic solvents depends on the edge configuration. If we compare the solvation energy of the ZZ-GQDs with that of the AC-GQDs, we see that the solubility is larger for the AC-GQDs. A partial desolvation of the GQDs in organic solvents leads to changes in their electronic properties. In particular, with increasing the solvent dielectric constant the HOMO level shifts towards more negative values for both types of GQDs. Since the HOMO energy is an indicator of the GQD ability to donate electrons to appropriate acceptors, then more negative HOMO energies imply easier and faster charge transfer process. In other words, GQDs dispersed in solvents with high dielectric constant are more reactive (more reactive sites are available for reaction) than those in the gas-phase. In addition, the absolute values of *E*HOMO of the AC-GQDs are slightly larger in comparison with those of ZZ-GQDs, suggesting a better reactivity and binding ability to possible adsorbates in the case of armchair-type edge termination. Despite the slight drop of the HOMO level in a polar solvent, the HOMO-LUMO gap and global hardness is less sensitive to dielectric permittivity. These findings open the way for tuning the reactivity of GQDs by controlling the dielectric permittivity of a solvent.

*Table S1. Computed parameters of zigzag- and armchair-edged GQDs immersed in different media*

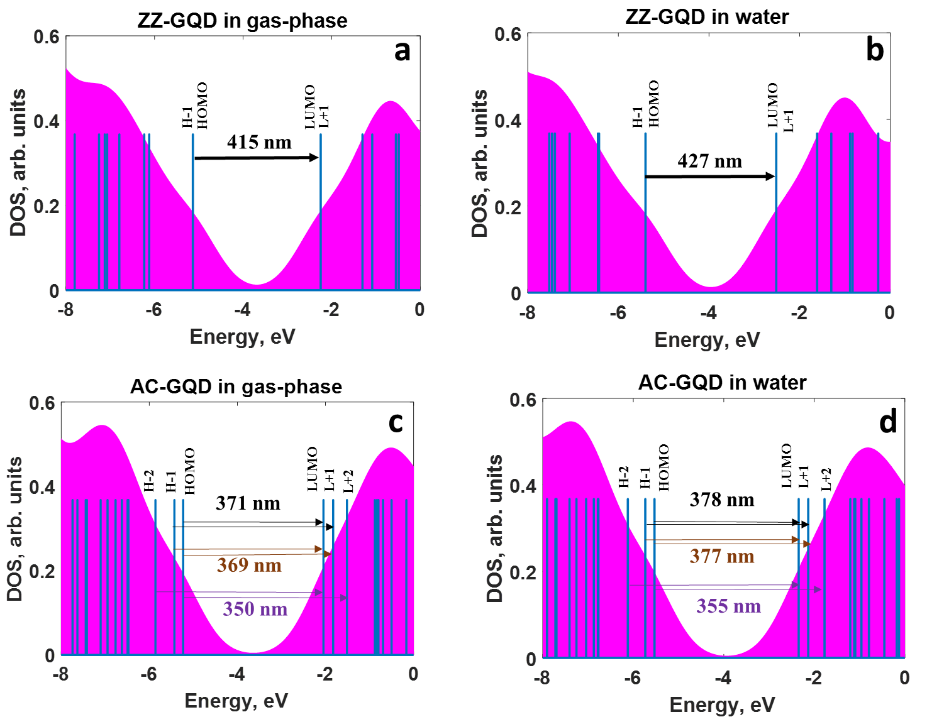
|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Parameter** | **Gas-phase**  ***ε*=1** | | **Acetic acid**  ***ε*=6.2528** | | **Ethanol**  ***ε*=24.852** | | **DMF**  ***ε*=37.219** | | **Water**  ***ε*=78.355** | |
| ***ZZ*** | ***AC*** | ***ZZ*** | ***AC*** | ***ZZ*** | ***AC*** | ***ZZ*** | ***AC*** | ***ZZ*** | ***AC*** |
| **|Cohesive energy|,eV** | 7.408 | 7.145 | 7.355 | 7.095 | 7.343 | 7.084 | 7.342 | 7.083 | 7.340 | 7.082 |
| **Solvation energy, eV** | - | - | -0.356 | -0.411 | -0.464 | -0.536 | -0.478 | -0.552 | -0.493 | -0.570 |
| **HOMO, Hartree** | -0.1886 | -0.1922 | -0.1954 | -0.1998 | -0.1978 | -0.2025 | -0.1981 | -0.2028 | -0.1984 | -0.2032 |
| **LUMO, Hartree** | -0.0826 | -0.0751 | -0.0893 | -0.0827 | -0.0917 | -0.0854 | -0.0921 | -0.0857 | -0.0924 | -0.0861 |
| ***E*HOMO-LUMO, eV** | 2.885 | 3.185 | 2.886 | 3.186 | 2.885 | 3.186 | 2.885 | 3.186 | 2.885 | 3.186 |
| **Electrophilicity, eV** | 4.722 | 4.155 | 5.203 | 4.641 | 5.381 | 4.817 | 5.405 | 4.840 | 5.431 | 4.866 |
| **Hardness, eV** | 1.442 | 1.592 | 1.443 | 1.593 | 1.442 | 1.593 | 1.442 | 1.593 | 1.442 | 1.593 |

The optical properties of the GQDs immersed in different media here are best represented by the absorption spectra. The absorption spectra of zigzag- and armchair-edged GQDs are presented in Figure S1. Each spectrum exhibits one intense absorption band at 415 nm for ZZ-GQDs and ~370 nm for AC-GQDs, respectively. As can be seen from Figure S1, the absorption wavelength of both ZZ-GQDs and AC-GQDs dispersed in solvents is red shifted as compared to those in the gas-phase (from 415 nm to 427 nm for ZZ-GQDs and from 370 nm to 378 nm for AC-GQDs, respectively). Furthermore, in both cases the absorption peak slightly increases in the intensity when passing from the gas-phase to solvents. The observed changes can be ascribed to the conductor-like screening effect, which is responsible for the appearance of the solvent-induced dipole moments and, as a consequence, for the modification of the configurations of the oscillators.4-6 Nevertheless, the absorption wavelengths and absorption intensities are almost similar in all considered solvents (acetic acid, ethanol, DMF and water). In fact, even the water, having the strongest polarity, has no significant effect on the optical properties of the graphene quantum dots in comparison to other solvents. To understand the origin of the absorption peaks we performed DOS calculations for both GQDs in different media. It was revealed that the HOMO−1 and HOMO as well as LUMO+1 and LUMO are degenerate π and π\* orbitals in zigzag-edged GQDs (Figs. S2a and S2b, respectively). This is because they have the same energies, orbital compositions, and occupancy. Figs. S2a and S2b also illustrate the transitions from the occupied states to the empty states (since all solvents demonstrate similar effect on the absorption spectra of the ZZ-GQDs, here we compare only results of DFT calculations in the gas-phase and water). Thus, the observed absorption spectra of the ZZ-GQDs are originating from multilevel lowest singlet transitions between degenerated orbitals. In other words, the corresponding spectra are dominated by four different transitions: HOMO → LUMO (46%) and H−1 → L+1 (46%); H-1→ LUMO (46%) and HOMO → L+1 (46%). Molecular orbitals, which are involved in these transitions are shown in Figure S1 (Electronic Supplementary Information #2).



*Figure S1. UV-vis absorption spectra of the pristine GQDs obtained in different dielectric media by using the PCM/TD-DFT/B3LYP/6-31G calculations of excited transitions: (left panel) zigzag edge termination and (right panel) armchair edge termination.*

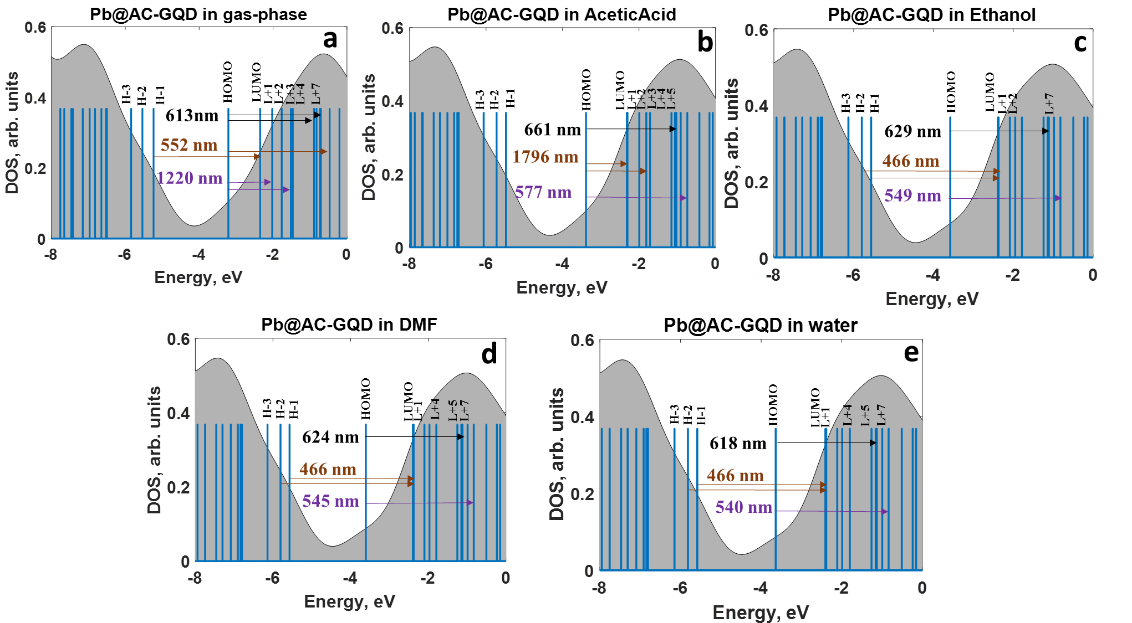
Contrary to the doubly degenerate LUMO and HOMO in ZZ-GQDs, the lowest orbitals in AC-GQDs split into two nondegenerate orbitals (see Figs. S2c and S2d, see also Figure S1, Electronic Supplementary Information #2). The splitting of the LUMO and HOMO is responsible for a change in the nature of the electronic excitations: from doubly degenerate HOMO→LUMO transition to two nondegenerate transitions (369 nm and 371 nm in gas-phase and 377 and 378 nm in water). Therefore, the absorption spectra of AC-GQDs are composed of two sets of transitions with similar oscillator strengths: H-1→ L+1 (75%), HOMO→ LUMO (16%) as well as H-1→ LUMO (46%), HOMO→ L+1 (48%). We find also a weak contribution of electronic excitation at 350 nm (355 nm in water) with an oscillator strength of *f*=0.326 (*f*=0.319 in water) to absorption spectra of the AC-GQDs. From the analysis of the electronic nature of this excitation, one can conclude that the dominant contribution to this transition arises from H-2→ LUMO and HOMO→ L+2. Tables S1 and S2 (Electronic Supplementary Information #2) summarize the electronic transitions, which contribute to the absorption spectra of the ZZ-GQDs and AC-GQDs immersed in different media.

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*Figure S2. DOS of pristine GQDs (shaded area) immersed in different media: (a) ZZ-GQD in the gas-phase, (b)* *ZZ-GQD in the water, (c) AC-GQD in the gas-phase, (d)* *AC-GQD in the water. Blue vertical lines denote the molecular orbitals. The excited transitions between available occupied and unoccupied electronic levels are shown by black arrowed lines.*

1. **Excited transitions in Pb0@AC-GQDs**

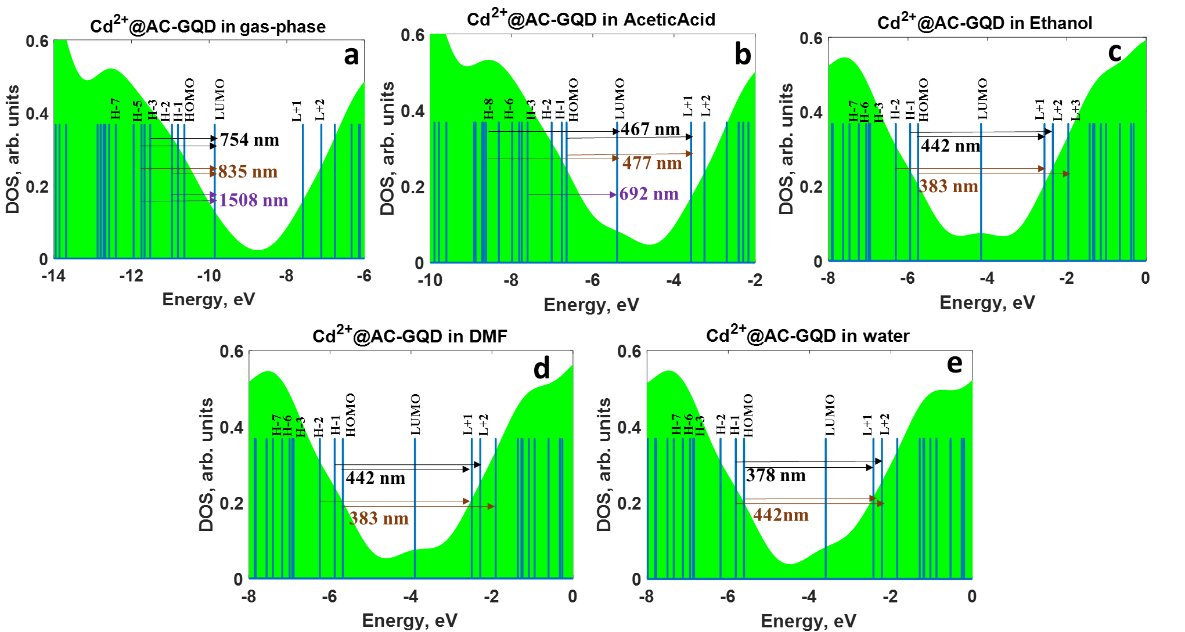
The solvent effect is significant also for the absorption properties of the armchair-edged GQDs interacted with neutral Pb adatom, as seen in Figure S3. This situation is very similar to the Pb0@ZZ-GQD case, confirming the solvent-induced absorption quenching in the wide wavelength range. Under vacuum conditions, a few transitions at 552, 613 and 1220 nm with very small oscillator strengths are dominated. These transitions come mainly from the three single excitations of HOMO→LUMO+9, HOMO→LUMO+7 and HOMO→LUMO+1, respectively. According to the orbital composition analysis, these orbitals seem to be hybrid and shared between Pb and AC-GQD (Figure S5, Electronic Supplementary Information #2). For Pb0@ZZ-GQD in the solvents, it was observed that the role of hybrid orbitals in electronic transitions is minimized and existing states with low oscillator strengths are mostly related to electron excitation from the HOMO level, which is almost localized on the Pb adatom (Figure S5, Electronic Supplementary Information #2). At the same time, the low-energy parts of the absorption spectra of the Pb0@AC-GQD in ethanol, water and DMF are dominated by two transitions at 466 nm: HOMO-2→LUMO and HOMO-1→LUMO+1, respectively. Among these orbitals, only LUMO+1 is hybrid, while the wave functions of HOMO-2, LUMO, HOMO-1 are completely distributed over the surface of AC-GQDs.

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*Figure S3. DOS of armchair-edged GQDs after complexation with Pb0 (shaded area) immersed in different media: (a) Pb0@AC-GQD in the gas-phase, (b) Pb0@AC-GQD in acetic acid, (c) Pb0@AC-GQD in the ethanol, (d) Pb0@AC-GQD in the DMF, and (e) Pb0@AC-GQD in the water. Blue vertical lines denote the molecular orbitals. The excited transitions between available occupied and unoccupied electronic levels are shown by black arrowed lines.*

1. **Excited transitions in Cd2+@AC-GQDs**

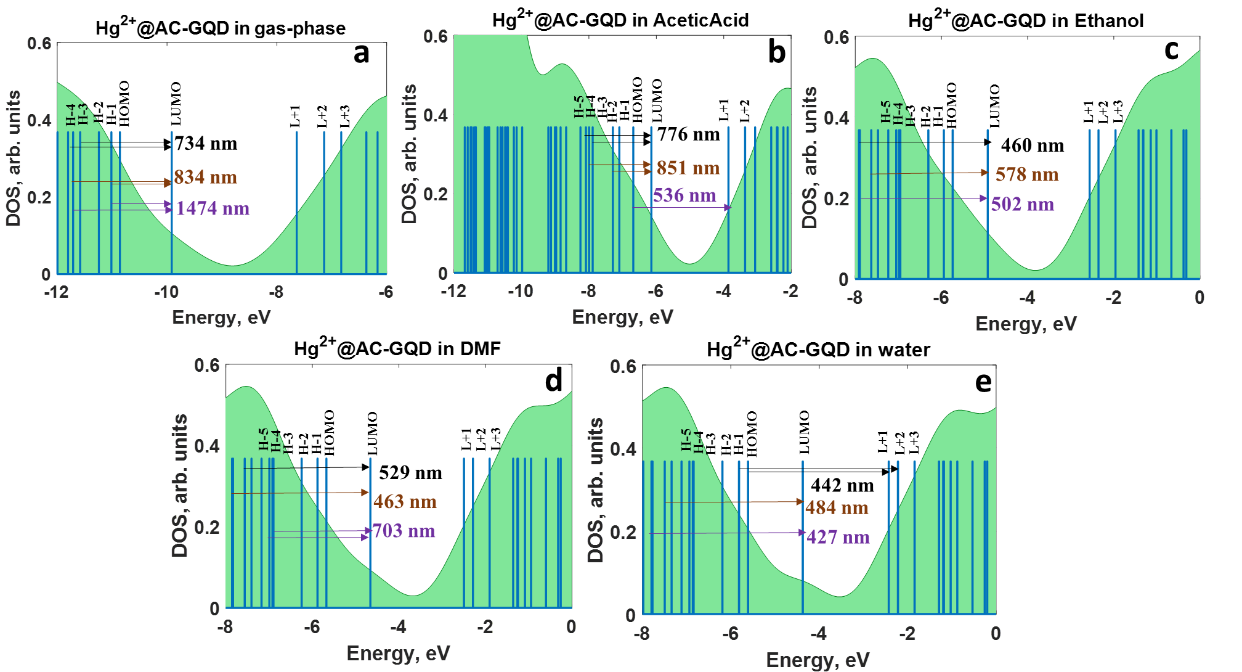
Moving from Cd2+@ZZ-GQD to the Cd2+@AC-GQD we see that similarly to the previous case the increase in the dielectric constant of the environment causes a significant HOMO-LUMO gap widening, followed by the blue-shift of the absorption peak. This is mainly due to the solvent-mediated weakening of the interaction strength in the Cd2+@AC-GQD combined system. It is also obvious that the absorption intensity under vacuum conditions is higher than that in acetic acid, ethanol and DMF. Only Cd2+@AC-GQD immersed in most polar solvent – water – exhibits the sharpest absorption peak. In the gas-phase, the absorption spectrum contains intense peaks at 754 and 835 nm and a weak feature at 1508 nm. It is interesting to note that the first two peaks are associated with transitions from the very close GQD-related energy levels HOMO-3, HOMO-4, HOMO-5 (forming the energy band) to LUMO level (Dataset S4, Electronic Supplementary Information #2). The contribution of Cd2+ to LUMO is only about 9 % (Figure S20, Electronic Supplementary Information #2). While the weak long-wavelength absorption band can be attributed to the single transition from HOMO-2 to LUMO. The assignments of the corresponding transitions are summarized for each cases in Table S6 (Electronic Supplementary Information #2) and Figure S4. Starting from the acetic acid, the contribution of the Cd2+ to LUMO increases from 79 % for acetic acid to 99 % for water and in the case of the most polar solvents this level is not able to participate effectively in electronic transitions with high oscillator strengths (Figure S4 c-e). The electronic spectrum of Cd2+@AC-GQD in acetic acid exhibits 3 bands at 467, 477 and 692 nm. The first two peaks are associated with the same transitions from the HOMO-8, HOMO to LUMO, LUMO+1, while third less intense feature at 692 nm can be assigned to HOMO-3→LUMO transition. We noticed the hybrid nature of the HOMO and LUMO+1 levels, with partial contribution of Cd as low as 9% and 3 %, respectively (see also Figure S20, Electronic Supplementary Information #2). The most notable result of replacing acetic acid by ethanol/DMF is the appearance of two dominating absorption features at 383 nm and 442 nm. The positions and intensities of these peaks are almost identical to each other. The band at 383 nm is therefore assigned to the following transitions (HOMO-2→LUMO+1 and HOMO→LUMO+3), while the most likely transitions contributing to 442 nm absorption are HOMO-1→LUMO+2 and HOMO→LUMO+1. In the aqueous environment, the first two lowest energy features observed at 378 and 442 nm 961.9 are dominated. Our calculations indicate that the transitions involving HOMO-1→LUMO+2 and HOMO→LUMO+1 molecular orbital transitions should be responsible for these peaks.

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*Figure S4. DOS of armchair-edged GQDs after complexation with Cd2+ (shaded area) immersed in different media: (a) Cd2+@AC-GQD in the gas-phase, (b) Cd2+@AC-GQD in acetic acid, (c) Cd2+@AC-GQD in the ethanol, (d) Cd2+@AC-GQD in the DMF, and (e) Cd2+@AC-GQD in the water. Blue vertical lines denote the molecular orbitals. The excited transitions between available occupied and unoccupied electronic levels are shown by black arrowed lines.*

1. **Excited transitions in Hg2+@AC-GQDs**

Next let's take a closer look at the assignments of the absorption features observed in Hg2+@AC-GQDs to the electronic transitions. Figure S5 illustrates the transitions from the occupied electronic states to the empty levels, which contribute to the first three most intensive peaks in the absorption curves of Hg2+@AC-GQDs dispersed in the different media. Based on the analysis of the existing transitions, one can observe that the dominant contribution to the most intensive peak at 734 nm arises from the HOMO-3→LUMO. Likewise, we associate the peak at 834 nm with two transitions: HOMO-4→LUMO (84 %) and HOMO-1→LUMO (10 %). The less intense peak near 1474 nm (with small oscillator strength of 0.05) exhibits a dominant contribution from HOMO-4→LUMO (10 %) and HOMO-1→LUMO (90 %) transitions. The orbital composition analysis provides the evidences that only GQD-related levels are involved in these transitions. Passing from the gas-phase to the acetic acid the absorption intensity remains almost unchanged. Nevertheless, the nature of the electronic transitions in Hg2+@AC-GQD dispersed in acetic acid becomes more complicated since hybrid HOMO (GQD: 17 %, Hg: 83 %) and LUMO (GQD: 85 %, Hg: 15 %) orbitals begin to participate in the excited transitions (Figure S22, Electronic Supplementary Information #2). In particular, the first most intensive peak at 776 nm is due to the combination of two close transitions, such as HOMO-5→LUMO (13 %) and HOMO-5→LUMO (85 %). The second peak near 851 nm is originating from HOMO-4→LUMO. The peak near 536 nm appears as a result of a single transition from the hybrid HOMO level to the LUMO+1 level. Similarly to the Hg2+@ZZ-GQD case, further increase in the dielectric constant of the solvent causes the localization of the LUMO level mainly on the Hg adsorbate, followed by the significant drop in the absorption intensity. It can be seen from Fig. S5 (c, d) and the Dataset S5 (Electronic Supplementary Information #2) that in the ethanol and the DMF the LUMO level is involved in all transitions, thereby leading to the vanishing of the oscillator strengths for the available transitions. On the other hand, being immersed in water solution Hg2+@AC-GQD demonstrates observable increasing of the absorption intensity. We can ascribe this increase to the non-symmetric nature of the armchair-edged GQD, which manifest itself in splitting the lowest occupied and highest unoccupied levels belonging to the GQD into a set of close energy levels. As an important consequence, the transitions from HOMO-1 to LUMO-2 and from HOMO to LUMO-1 become allowed and generate the absorption features at 442 nm.

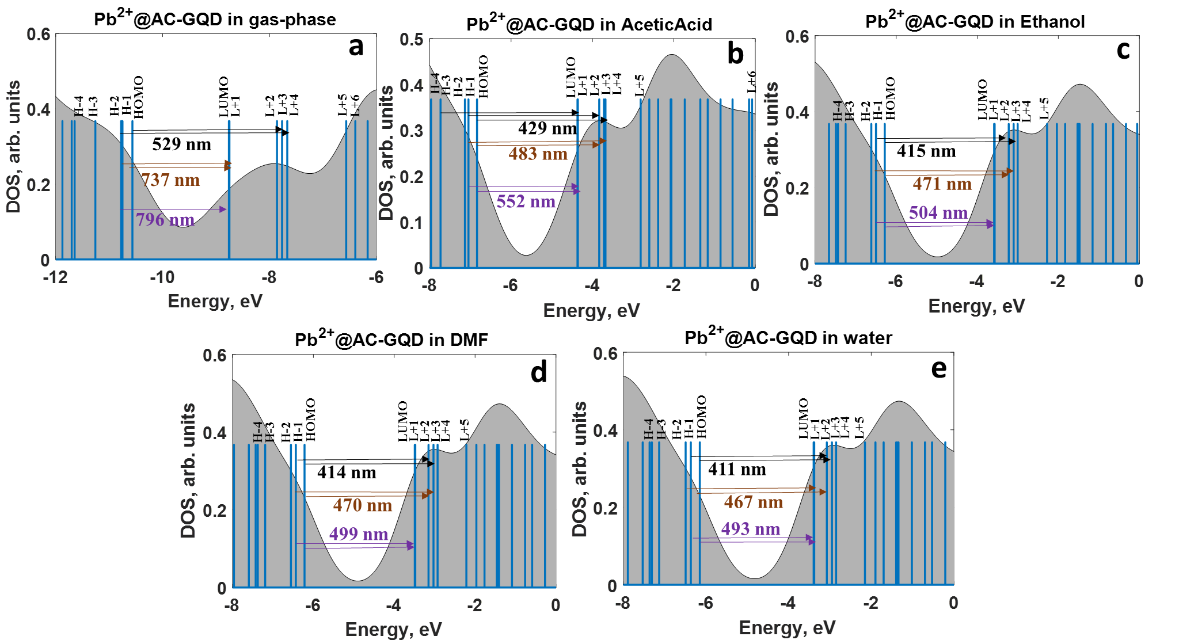
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*Figure S5. DOS of armchair-edged GQDs after complexation with Hg2+(shaded area) immersed in different media: (a) Hg2+@AC-GQD in the gas-phase, (b) Hg2+@AC-GQD in acetic acid, (c) Hg2+@AC-GQD in the ethanol, (d) Hg2+@AC-GQD in the DMF, and (e) Hg2+@AC-GQD in the water. Blue vertical lines denote the molecular orbitals. The excited transitions between available occupied and unoccupied electronic levels are shown by black arrowed lines.*

1. **Excited transitions in Pb2+@AC-GQDs**

Drawing our attention to the absorption spectra of the Pb2+@AC-GQD, in the following we gain insights into the origin of the electronic transitions in the presence of the solvent environment. The peaks’ assignment is presented in Fig. S6. In the absorption spectrum of Pb2+@AC-GQD in the gas-phase three weak bands at 529, 737 and 796 nm can be observed. The first feature at 529 nm is mainly assigned to the transition between the HOMO and the LUMO+3 level (with slight contribution of other transitions: HOMO-4→LUMO, HOMO-1→LUMO+4). Interestingly, both HOMO and LUMO+3 are mostly GQD-related occupied and unoccupied levels, respectively. The second peak at 737 nm can be identified as overlapped multi-level transition, including contributions from HOMO-2→LUMO+1, HOMO-1→LUMO and HOMO→LUMO+1, respectively. In this case, hybrid LUMO and Pb-related LUMO+1 levels are involved in the excited state. The third peak with small oscillator strength of 0.0203 is mainly attributed to the HOMO-2→LUMO transition. Similarly to the Pb2+@ZZ-GQD case, the solvent effect is most pronounced on the absorption wavelengths and absorption intensities in Pb2+@AC-GQD. As was mentioned before, we explain this phenomena by the solvent-induced weakening of the electrostatic interaction between Pb2+ and AC-GQD. In particular, a clear blue-shift of the most prominent absorption peaks can be seen in Fig. S6 (b-e). Passing from the gas-phase to acetic acid, we noticed that the absorption spectrum of the Pb2+@AC-GQD is mainly composed of three bands at 429, 483 and 552 nm, respectively. A detailed analysis of the calculated results indicates that three transitions contribute to the most intense peak at 429 nm, including HOMO-3→LUMO (33 %), HOMO-1→LUMO+2 (39 %) and HOMO→LUMO+3 (22%). These transitions contribute almost equally to the aforementioned absorption peak. While the contribution of the Pb2+ to the HOMO, HOMO-1, and HOMO-3, LUMO+2 and LUMO + 3 is found to be negligibly small, the contribution of Pb2+ ion to LUMO orbital reaches ~87% (Figure S24, Electronic Supplementary Information #2). Figure S6b illustrates the contributing orbitals, which are involved in the corresponding transitions. Another feature at 483 nm is mainly related to the mixture of two transitions: HOMO-1→LUMO+3 (13 %), HOMO→LUMO+2 (85 %). Finally, the small absorption peak at 552 nm is attributed to HOMO-1→LUMO (85 %), HOMO→LUMO+1 (14 %), respectively. For the LUMO-1, the contribution of the divalent ion is approximately 88 %.

Further increase of the dielectric constant of the solvent leads to a subsequent shift of the absorption peak of Pb2+@AC-GQD towards the short-wavelength side and an enhancement of the absorption intensity, as is seen in Fig. S6(c-e). Analysing the spectra of the interacting systems immersed in the polar solvents (ethanol, DMF and water), we did not reveal a large difference between the absorption curves. In other words, the same molecular orbitals are involved in the electronic transitions in Pb2+@AC-GQD. Considering the absorption spectrum in water one can see that three bands at 411, 467 and 493 nm can be distinguished. The first absorption peak of Pb2+@AC-GQD in water at 411 nm can be identified as a combination of two transitions: HOMO-1→LUMO+2 (54 %) and HOMO→LUMO+3 (32 %), respectively. The electron density for these orbitals is delocalized over the planar surface of the AC-GQD, while the central Pb2+ has negligible contribution. Another peak at the 467 nm is related to the following transitions: HOMO→LUMO+2 (72 %), HOMO-2→LUMO (13 %) and HOMO-1→LUMO+3(13 %), respectively. The Pb2+ ion is contributing only to LUMO (87 %). The last feature at 493 nm is dominated by two transitions from the π-symmetric GQD-related occupied levels to double degenerate lowest unoccupied levels: HOMO→LUMO+1 (84 %), HOMO-1→LUMO (11 %).

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*Figure S6. DOS of GQDs after complexation with Pb2+ (shaded area) immersed in different media: (a) Pb2+@AC-GQD in the gas-phase, (b) Pb2+@AC-GQD in acetic acid, (c) Pb2+@AC-GQD in the ethanol, (d) Pb2+@AC-GQD in the DMF, and (e) Pb2+@AC-GQD in the water. Blue vertical lines denote the molecular orbitals. The excited transitions between available occupied and unoccupied electronic levels are shown by black arrowed lines.*

1. **Side effect on the binding energy of HMs and optical properties of the interacting systems**

We considered and compared two different adsorption situations: (i) HMs are adsorbed onto the carbon atoms at the edges of the GQDs and (ii) HMs are adsorbed above the middle area of the GQDs. We revealed that there is no large difference in binding energies of the Cd and Hg adatoms in these two adsorption configurations (Figure S7). In the case of the Pb adsorption the side effect is much more pronounced in comparison to adsorption events involving other metals (Figure S7). In particular, the binding energy significantly increases due to the side effect. This can be explained by the fact that Cd and Hg adatoms always tend to sit on the hollow site, thereby moving from the initial edge position to the center of the closest hexagonal ring (Table S9, Electronic Supplementary 2). While Pb adatom prefers to sit at one of the bridge sites at the edges of GQDs. In fact, these positions are more energetically favorable than the bridge sites in the central part of the GQDs. Furthermore, Pb adatom interacts with armchair-edged GQD in stronger manner than with zigzag-edged GQDs. These results manifests themselves in optical properties of the metal-GQD complexes. In particular, the absorption spectra of the GQDs interacted with Cd and Hg adatoms are the same for both configurations, while the excited transitions in Pb@GQD are sensitive to the Pb adsorption site (See the Figure S8). It is interesting note that the binding energies of divalent metal ions undergo no significant change with changing the adsorption sites from middle area to edge regions (Figure S9). At the same time, Cd2+@GQD, Hg2+@GQD and Pb2+@GQD complexes exhibit behavior similar to those involving the neutral metal adatoms (Figure S10). We speculate that the main cause for the variations in absorption intensity of the Pb@GQD and Pb2+@GQD can be related to the side effect. In principle, being adsorbed at the edges of GQDs, Pb species can donate electrons only to the edge carbon atoms, thereby increasing the area of adsorbate-free region in the middle part of the GQDs. As a result, the existence of the non-disturbed area of the *sp*2 plane contributes mainly to the enhanced absorption in the visible region. Therefore, we observed an increase in the oscillator strengths of the main transitions in Pb@GQD and Pb2+@GQD when Pb species are located the edges of the GQDs.



*Figure S7. Binding energies of neutral HM adatoms on (a) zigzag-edged and (b) armchair-edged GQDs in the gas-phase obtained using B3LYP/6-31g level of theory.*



*Figure S8 Absorption spectra of the GQDs after complexation with different heavy metals: (a) Cd@ZZ-GQD, (b) Hg@ZZ-GQD and (c) Pb@ZZ-GQD; d) Cd@AC-GQD, (e) Hg@AC-GQD and (f) Pb@AC-GQD. Two adsorption configurations are considered for comparison. The spectra were calculated using B3LYP/6-31g level of theory.*



*Figure S9. Binding energies of divalent HM ions on (a) zigzag-edged and (b) armchair-edged GQDs in the gas-phase obtained using B3LYP/6-31g level of theory.*



*Figure S10 Absorption spectra of the GQDs after complexation with different heavy metals: (a) Cd2+@ZZ-GQD, (b) Hg2+@ZZ-GQD and (c) Pb2+@ZZ-GQD; d) Cd2+@AC-GQD, (e) Hg2+@AC-GQD and (f) Pb2+@AC-GQD. Two adsorption configurations are considered for comparison. The spectra were calculated using B3LYP/6-31g level of theory.*

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