Supplementary Information

IR and Raman Spectroscopy Reveal Amino Acid–Surface Interactions on B- and N-Doped Hydroxylated Graphene Quantum Dots: A DFT Study

Berke Özgür Arslan, Mine Yurtsever*

Detailed Analyses of IR Spectra of the Studied GQDs

1. The change in the IR spectrum of Pristine GQD (G) due to covalent OH functionalization.

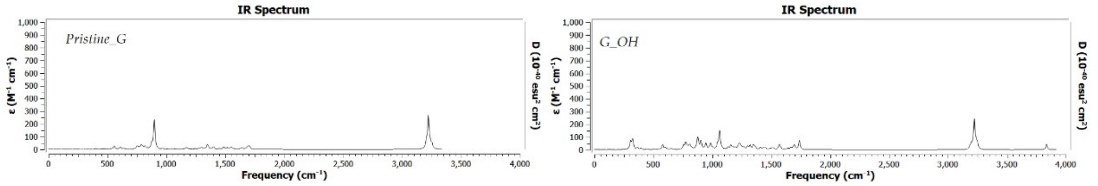


Figure S1a. The IR spectra of pristine (G) and OH-functionalized (G-OH) GQD surfaces.

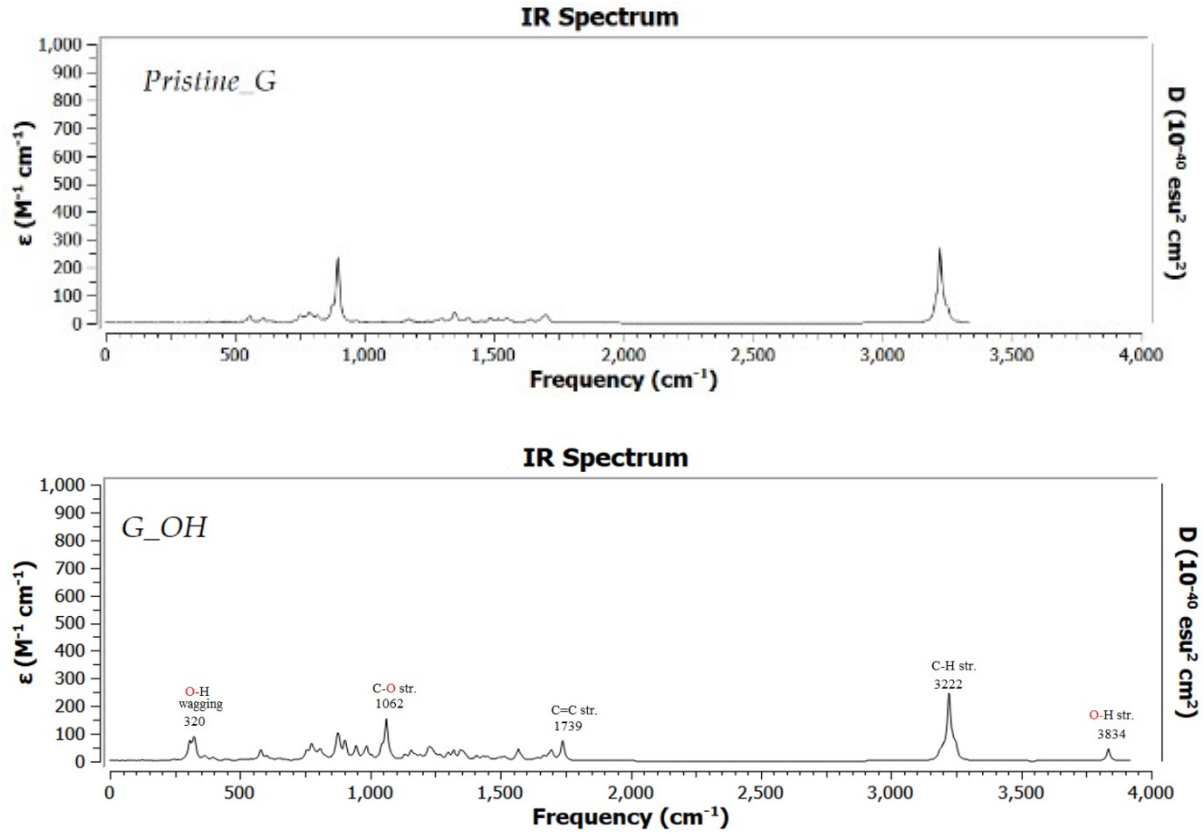


Figure S1b. The zoomed-out IR spectra of pristine (G) and OH-functionalized (G-OH) GQD surfaces.

* Corresponding Author (mine@itu.edu.tr)

All harmonic vibrational frequencies computed at the M06-2X level are typically scaled by 0.955 to account for systematic anharmonicity and basis set limitations.

In this study, although harmonic frequencies were not explicitly scaled, the comparison with experiment is based on vibrational regions and relative frequency shifts, which are less sensitive to systematic overestimation.

Table S1. Detailed IR Comparison (Pristine G vs G_OH)

Vibrational Region (cm^{-1})	Pristine GQD (G)	OH-Functionalized (G-OH)	Assignment	Interpretation
3200–3600 cm^{-1}	Absent	Broad strong band	O–H stretching	Confirms OH binding. H-bonding broadens the band.
1500–1700 cm^{-1}	Dominant C=C peak	Shifted C=C + changes	Aromatic C=C stretch	π-system perturbed by OH.
1200–1400 cm^{-1}	Moderate peaks	Enhanced intensity	C–O stretch	Formation of C–O bonds at edges/defects.
<1000 cm^{-1}	Graphene skeletal modes	Additional deformation peaks	C–O–H bending	New out-of-plane modes due to OH.

2. The Dopant Effect on IR Spectra of OH-Functionalized Surfaces

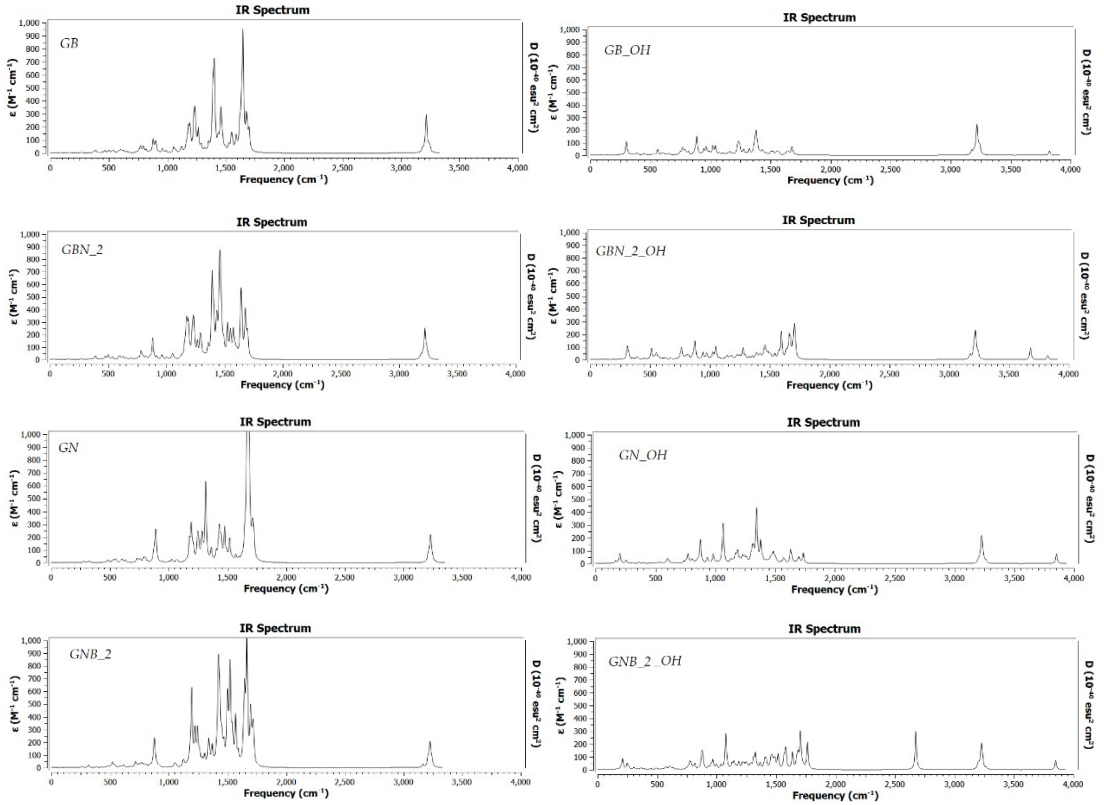


Figure S2. The IR spectra of doped and OH-functionalized GQD surfaces.

Table S2. Detailed IR Comparison (G_OH vs GNB_OH vs GBN_OH)

Vibrational Region	G_OH	GNB_OH	GBN_OH	Assignment	Interpretation
3200–3600 cm^{-1}	OH stretch	Shifted OH	Differently shifted OH	O–H stretching	Dopant environment modifies OH vibration.
1400–1600 cm^{-1}	C=C baseline	Lower-shifted peaks	Different shifts	C=C / C–N / B–N	Dopant positional changes alter electronic structure.
1100–1300 cm^{-1}	C–O, C–C	New modes	Different new modes	B–O & N–O	The proximity of dopants changes the bonding environment.

700–1000 cm^{-1}	Graphene modes	Additional peaks	Shifted additional peaks	B–C / N–C bending	The low-frequency region is very sensitive to the dopant position.

3. The impact of the positions of N and B dopant atoms on the IR spectra of the OH-functionalized surface.

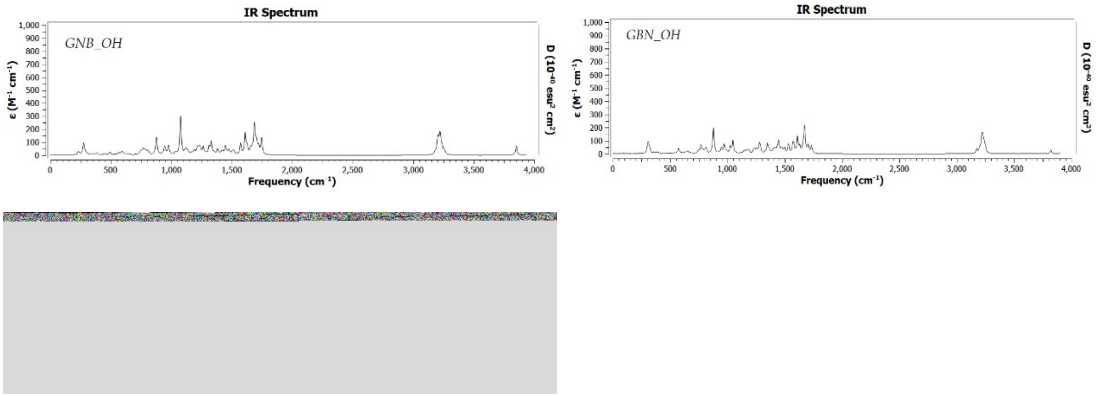


Figure S3*. Comparison of the IR spectra of the G_OH, GNB_OH, and GBN_OH structures regarding the exchange of the positions of the dopant atoms.*

G_OH displays a stronger, broader O–H stretching band centered around 3200–3500 cm^{-1}, indicating a stronger hydrogen bonding. In contrast, the GNB_OH and GBN_OH exhibit more intense, structured absorptions in the 1000–1750 cm^{-1} fingerprint region, typical of C=O and C–O stretches, consistent with altered substitution at graphitic edges. These differences indicate that N and B-doped G_OH are more extensively oxygen-functionalized than G_OH, while G_OH retains comparatively more free hydroxyl character.

Table S3. Detailed IR Comparison (G_OH vs GNB_OH vs GBN_OH)

Vibrational Region (cm^{-1})	G_OH	GNB_OH	GBN_OH	Assignment	Interpretation
3200–3600	**Strong, broad**	Medium, broad	Medium, broad	O–H stretch	G_OH shows the largest OH band due to stronger H-bonding.
~1750–1680	Weak	**More pronounced**	**More pronounced**	C=O stretching	Stronger high-frequency fingerprint absorptions are consistent with increased carbonyl content caused by doping
.1300–1000	Moderate	**Stronger**	**Stronger**	C–O stretching (phenolic)	GNB/GBN have enhanced intensity due to higher content of C–O functionalities

4a. Changes in the IR spectrum of glycine upon adsorption onto the OH-functionalized GQD surface.

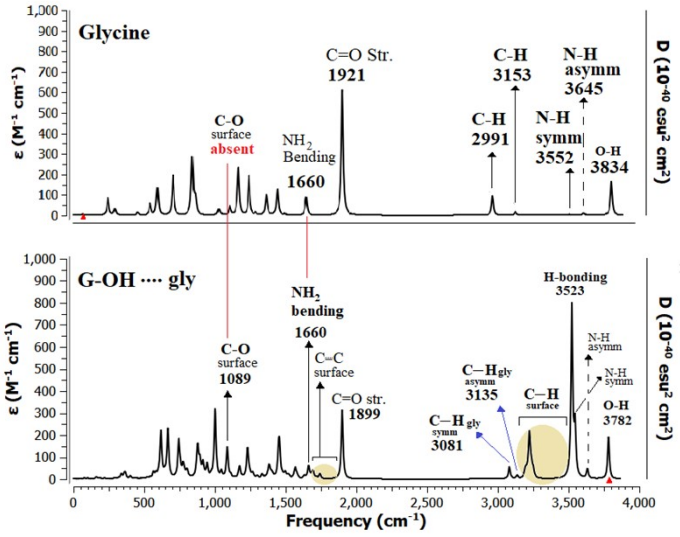


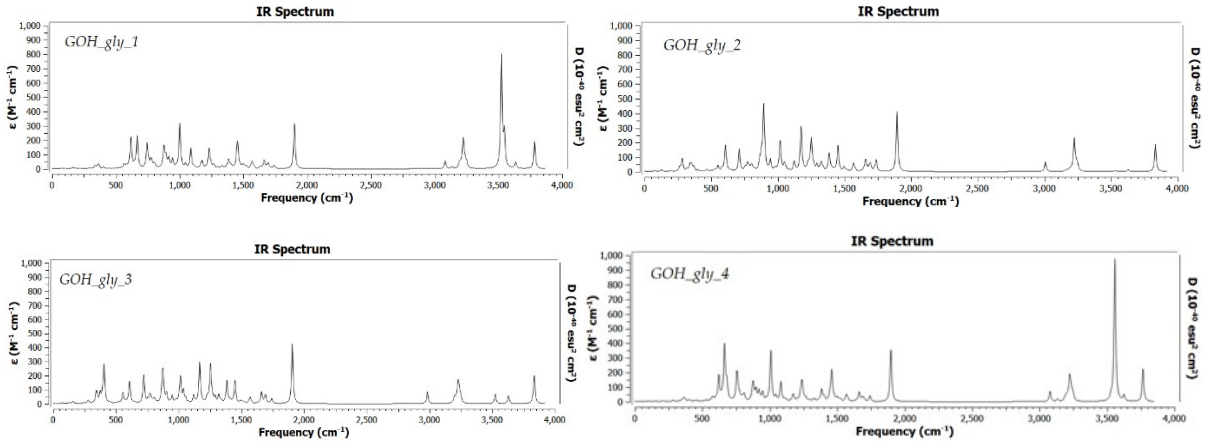
Figure S4a. Comparison of the IR spectra of glycine and OH-functionaized surface adsorbed glycine.

Compared with free glycine, the G–OH···glycine complex shows pronounced red shifts in the C=O and O–H stretching modes, the emergence of surface-specific C–O vibrations, and significant broadening of the N–H stretching region, collectively confirming hydrogen-bond-driven adsorption dominated by the carboxyl group.

Table S4a. Detailed IR Comparison (G_OH vs free Glycine)

Vibrational Mode	Free glycine (cm^{-1})	G–OH···gly (cm^{-1})	Interpretation
C=O stretch	1921	1899	**H-bonding,** bond weakening
NH_2 bending	1660	1660	no change
C–O (surface)	absent	1089	**Adsorption fingerprint**
C–H sym	2991	3081	Restricted motion
C–H asym	3153	3135	Electronic perturbation
N–H stretch	3552–3645	broadened	H-bond coupling
O–H stretch	3834	3782	Red shifted due to surface H-bonding

4b. The impact of the different Glycine conformations on the IR spectra of the OH-functionalized surface.



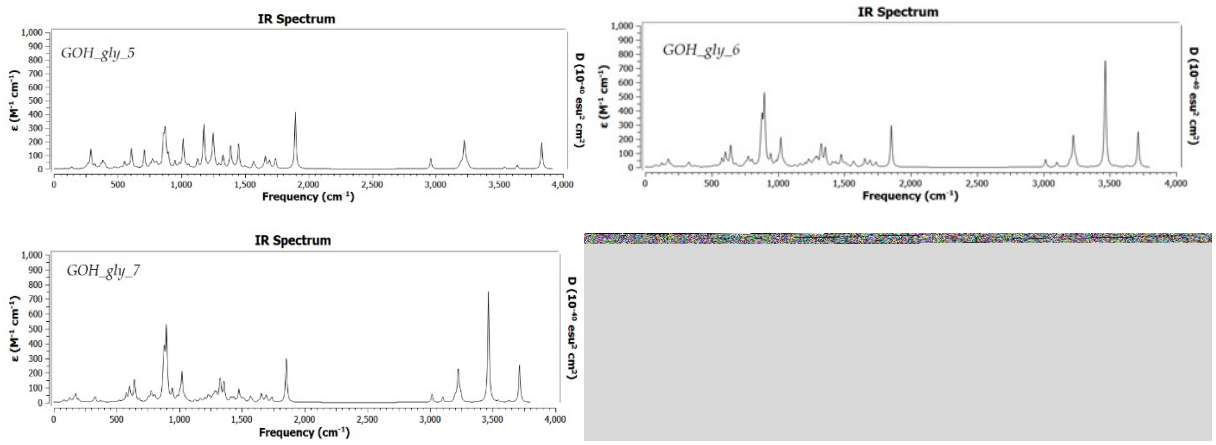


Figure S4b. *Comparison of the IR spectra of GOH_gly regarding different conformations (1-7) of glycine on the surface.*

Table S4b. Detailed IR Comparison (GOH_gly conformers 1–7)

Vibrational Region	Conformer Variability	Assignment	Interpretation
3200–3500 cm^{-1}	Small N–H stretch shifts	N–H stretch	H-bond strength varies with orientation.
2800–3000 cm^{-1}	Minor intensity changes	C–H stretch	CH_2 orientation is slightly different.
1600–1700 cm^{-1}	C=O peak shifts	C=O stretch	Orientation affects C=O–surface interaction.
1400–1550 cm^{-1}	COO^- modes shift	COO^- asymmetric/symmetric	Charge delocalization changes per conformation.
1000–1300 cm^{-1}	Intensity variations	C–N & C–O	Sensitive to torsional geometry.
<900 cm^{-1}	Distinct pattern shifts	Bending modes	Surface binding alters out-of-plane vibrations.

Due to non-covalent interactions between the amino acid and the surface, where an H-bond forms with the hydrogen of the OH functional group and the nitrogen atom of glycine, the O-H stretching frequency at 3834 cm^{-1} shifts to a lower frequency around 3700-3750 cm^{-1} and becomes more prominent. The newly formed high-intensity N-H stretching band in the 3000-3450 cm-1 region is strongly influenced by the strength of the H-bond between the surface and the adsorbed amino acid, showing orientation-dependent changes.

5. Impact of the type of amino acid on the IR spectra of the OH-functionalized surface.

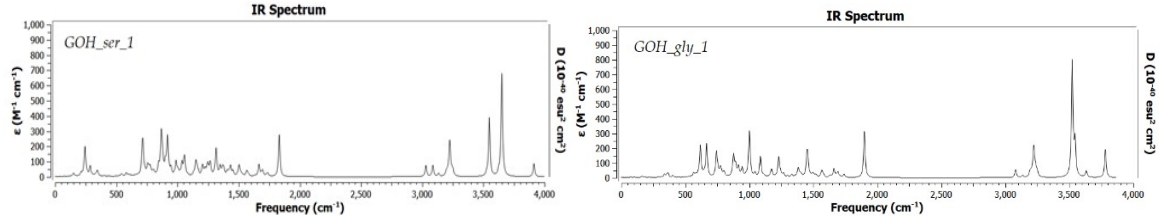


Figure S5. *Comparison of the IR spectra for GOH-ser and GOH_gly.*

Table 5. Detailed IR Comparison (GOH_gly vs GOH_ser)

Vibrational Region	GOH_gly	GOH_ser	Assignment	Interpretation
3200–3600 cm^{-1}	NH + one OH	NH + two OH	O–H & N–H stretch	Serine adds extra complexity due to the OH side-chain.
1600–1700 cm^{-1}	Single C=O peak	Shifted & stronger C=O	C=O stretch	Stronger adsorption of serine.
1400–1500 cm^{-1}	Moderate COO^-	More intense COO^-	COO^- stretching	Serine interacts more strongly.
1100–1300 cm^{-1}	C–N / C–O	Additional C–O from the side chain	Alcohol C–O, amine C–N	Side-chain OH introduces new features.
<1000 cm^{-1}	Simple bending patterns	More complex modes	CH/NH/OH bending	More flexible serine vibrational coupling.

The IR spectra of GOH_ser and GOH_gly show the same general features due to their shared graphene oxide backbone, but several characteristic differences arise from the distinct amino acid types. GOH_ser exhibits a broader O–H/N–H stretching band (3600–3200 cm^{-1}) and additional C–O stretching peaks (1200–1050 cm^{-1}), consistent with serine's hydroxyl-containing side chain. In contrast, GOH_gly lacks a side-chain hydroxyl and shows a sharper N–H/O–H region and weaker C–O bands. Slightly stronger C–H and amide II (1650–1550 cm^{-1}) bands in GOH_ser also reflect the increased surface interactions introduced by serine compared with glycine.

6. Comparison of IR Spectra of the Undoped G, G_OH, and G_OH_ser Structure

Figure S6. *Comparison of the IR spectra for G, G_OH, and GOH-ser*

Table S6. Detailed IR Comparison (G vs G_OH vs GOH_ser)

Vibrational Region	G	G_OH	GOH_ser	Assignment	Interpretation
3200–3600 cm^{-1}	Absent	O–H band	O–H + N–H bands	O–H, N–H stretches	Serine introduces additional NH & OH features.
1500–1700 cm^{-1}	C=C peaks	Shifted C=C	Extra strong peaks	C=O, C=N, C=C	Serine C=O creates new modes.
1100–1400 cm^{-1}	Graphene baseline	C–O modes	More complex C–O/C–N	C–O, C–N	Serine binding is evident.
<1000 cm^{-1}	Pure graphene bending	OH bending	Many new bends	NH/OH/CH bending	Strong serine–surface coupling.

7. Comparison of IR spectra of the GB and GB_OH structures

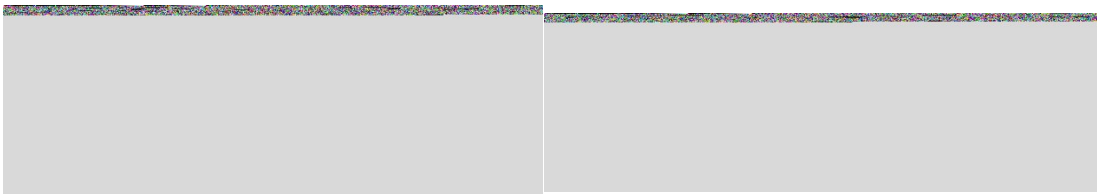


Figure S7. *Comparison of the IR spectra for GB, GB_OH*

Table S7. Detailed IR Comparison (GB vs GB_OH)

Vibrational Region(cm^{-1})	GB (B-Doped GQD)	GB_OH (Hydroxylated B-Doped GQD)	Interpretation
O–H stretching (3200–3600)	Absent	Strong broad band at ~3500–3600	Confirms addition of surface –OH groups; stronger hydrogen-bonding environment
C–H stretching (2800–3100)	Very weak	Unchanged	Indicates minimal sp^3-C formation; hydroxylation does not significantly introduce aliphatic C–H
C=C (sp^2) stretching (1500–1650)	Strong, sharp peaks around 1500–1600	Peaks are still present but slightly reduced in intensity	Hydroxylation disturbs π-conjugation; partial loss of aromatic character near functionalized sites
C–O stretching (1000–1300)	Weak	Stronger, more defined peaks around 1000–1200	Direct evidence of surface C–O bond formation following hydroxylation
Fingerprint region (600–1000)	Clear, structured	Broader, less intense	Structural disorder increases upon hydroxylation
Overall intensity	Higher intensity near 1500–1700	More distributed intensities with a dominant O–H band	Indicates reorganization of electron density; surface becomes more polar

Both spectra show the same underlying graphitic/aromatic backbone (clear mid-IR structure in the fingerprint and weak C–H stretches), but GB has very strong, sharp absorptions in the ~1200–1700 cm^{-1} region while GB_OH shows those bands strongly reduced and a broader O–H / O–H-related envelope in the 3200–3600 cm^{-1} region plus relatively stronger C–O features in the 1200–1000 cm^{-1} range. This pattern indicates that GB is more conjugated, whereas GB_OH is more oxygenated, with increased surface hydroxyl (and C–O) functionality, and the sharp conjugated modes weaken.

8. The Definition of the dopant positions

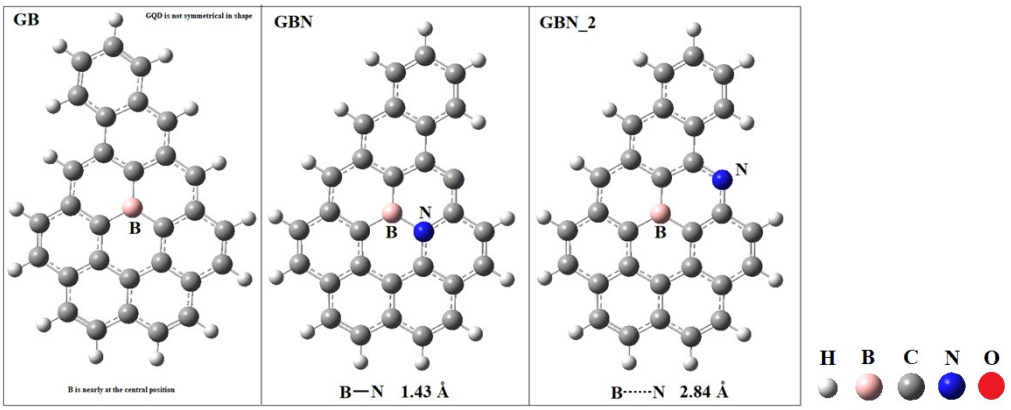


Figure S8. *The lattice positions of the dopant atoms*.

The relative positions of the dopant atoms govern the local charge distribution within the graphene quantum dots and are directly reflected in the vibrational response. In the GB structure, central boron substitution introduces a localized electron deficiency in the π-framework, weakening adjacent C–C bonds and leading to red shifts in graphene-derived

stretching modes with enhanced IR intensities. When boron and nitrogen are placed adjacently in GBN (B–N = 1.43 Å), donor–acceptor charge compensation between N and B partially restores local π-electron density, resulting in smaller frequency shifts of the C–C modes and the appearance of dopant-associated vibrational features with increased polarity-driven IR activity. In contrast, spatially separated dopants in GBN_2 (B···N = 2.84 Å) act as independent perturbation centers, producing a more heterogeneous charge distribution that manifests as broader shifts and splitting of C–C and C–O bands and more pronounced changes in Raman intensities. These trends demonstrate that dopant proximity controls charge localization and polarization, thereby dictating the observed IR and Raman spectral signatures.