

Supplementary information

Unravelling Chemical Heterogeneity and Dual Emission Pathways in Graphene Quantum Dots via Single-Particle Infrared Spectroscopy

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Section 1. AFM analysis

Sample Preparation

A colloidal dispersion of the sample in DI water was first prepared at a concentration of 1.1 mg/mL. This solution was then ultrasonicated for 30 minutes. Meanwhile, the top layer of the mica substrate was cleaved using adhesive tape. Subsequently, the solution was drop-cast onto the freshly cleaved mica. Finally, the substrate with the deposited sample was ultrasonicated for an additional 10 minutes to ensure well-distributed particles on the substrate.

Spatial Resolution of the PiFM

The Vista One PiFM equipment from Molecular Vista has a spatial resolution (topography) limited by the tip radius of curvature and the AFM scanner precision. As mentioned in the main document, the tip radius of curvature is 67 nm and, the scanner precision of the x, y and z axes is 100 pm RMS. Lateral resolution (xy) is limited by the tip shape and the features of the sample, the GQDs and NGQDs were placed on a flat surface, which helps with the lateral measurements; once the tip convolution is considered, an approximation of the true size can be resolved. Height resolution is only limited by the AFM scanner precision. In our samples, ~100 pm RMS is precise enough to measure sub-10 nm heights.

Small GQDs

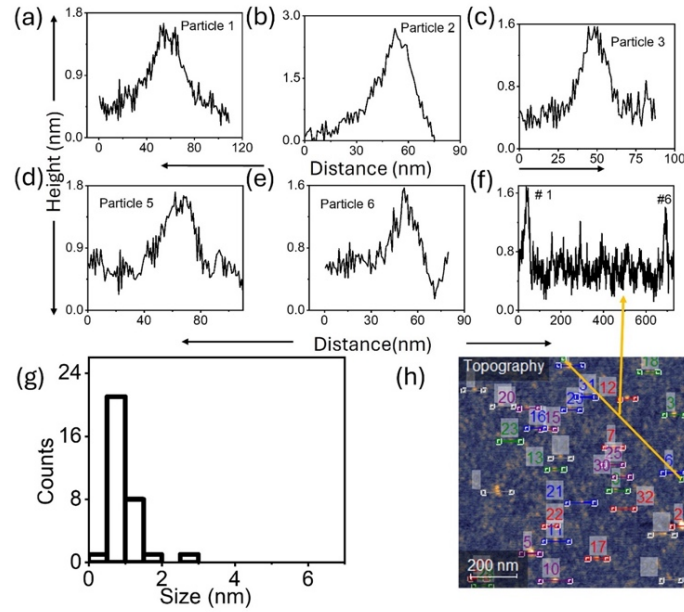


Figure S1: Particle height analyses of small GQDs. (a-e) Height profile of selected particles; (f) line profile over the chrome line indicated in (h) containing particle #1 and particle #6 as marked in the AFM micrograph; (g) histogram showing the height distribution of the particles analysed; (h) AFM image with particle numbers and lines of small GQD.

Medium GQDs

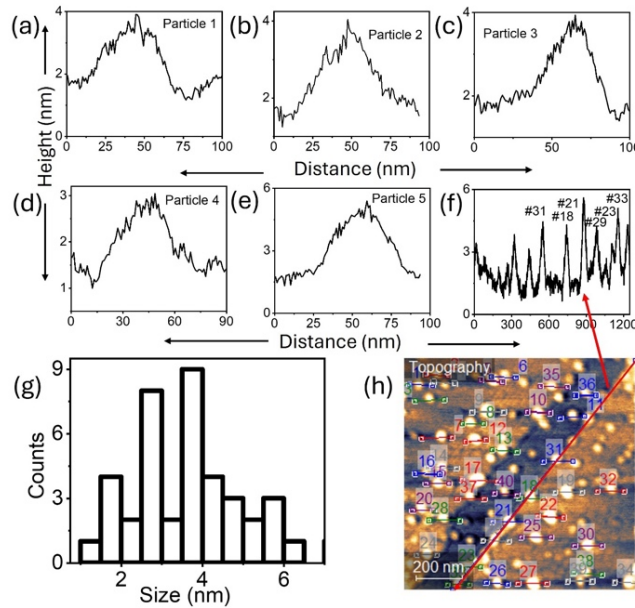


Figure S2: Particle height analyses of medium GQDs. (a-e) Height profile of selected particles; (f) line profile over the red line indicated in (h) containing several particles out of which particle #31, #18, #2, #29, #23 and #33 (as marked in the AFM micrograph) are indicated for easy reference; (g) Height distribution histogram of the particles; and (h) AFM image with particle numbers and lines.

Large GQDs

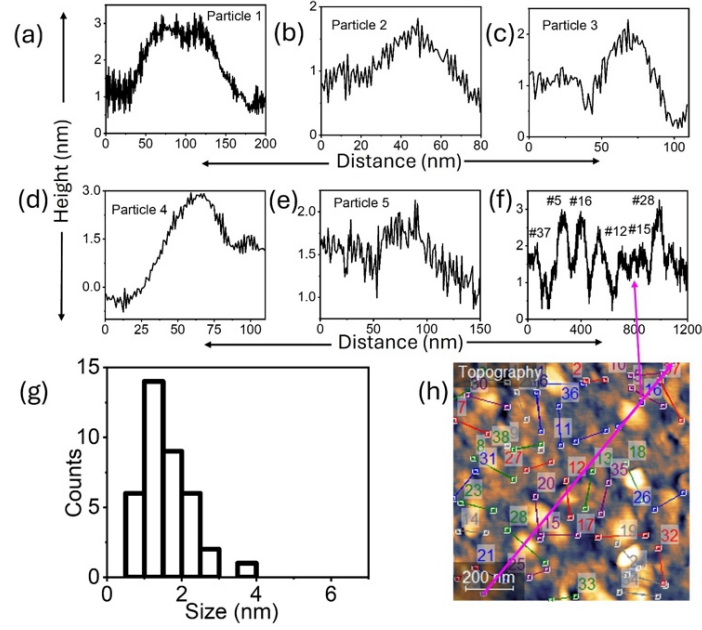


Figure S3: Particle height analyses of large GQDs. (a-e) Height profile of some selected particles, (f) line profile over the pink line indicated in (h) containing several particles out of which particle #28, #15, #12, #16, #5 and #37 (as marked in the AFM micrograph) are indicated for easy reference, (g) histogram showing the height distribution of the particles; and (h) AFM image with particle numbers and lines of large GQD.

Small NGQDs

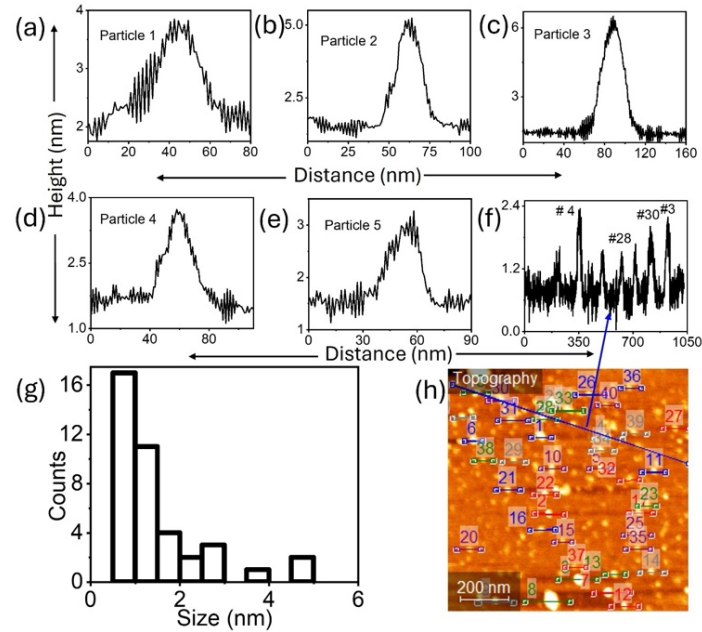


Figure S4: Particle height analyses of small NGQDs. (a-e) Height profile of selected particles, (f) line profile over the blue line indicated in (h) containing several particles out of which particle #3, #4, #28 and #30 (as marked in the AFM micrograph) are indicated for easy reference, (g) histogram showing the height distributions of the particles; and (h) AFM image with particle numbers and line.

Medium NGQDs

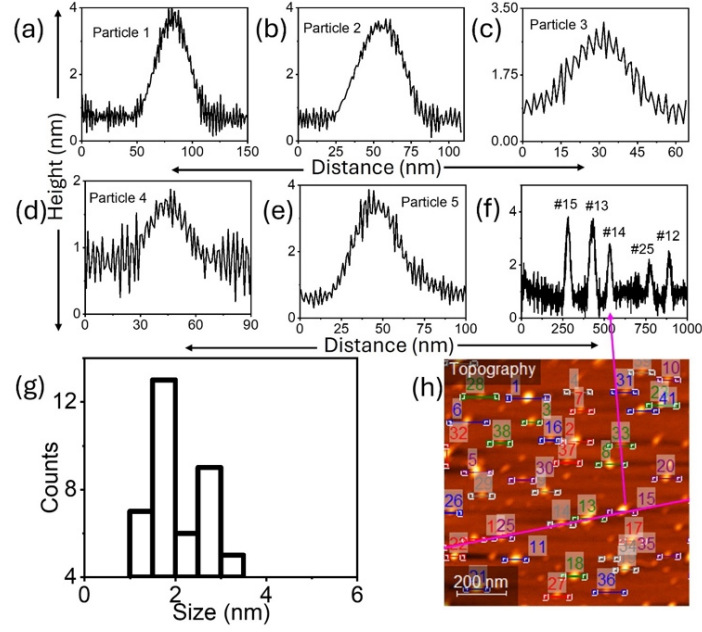


Figure S5: Particle height analyses of medium NGQDs. (a-e) Height profile of selected particles, (f) line profile over the pink line indicated in (h) containing several particles out of which particle #15, #13, #14, #25 and #12 (as marked in the AFM micrograph) are indicated for easy reference and (h) AFM image with particle numbers and lines.

Large NGQDs

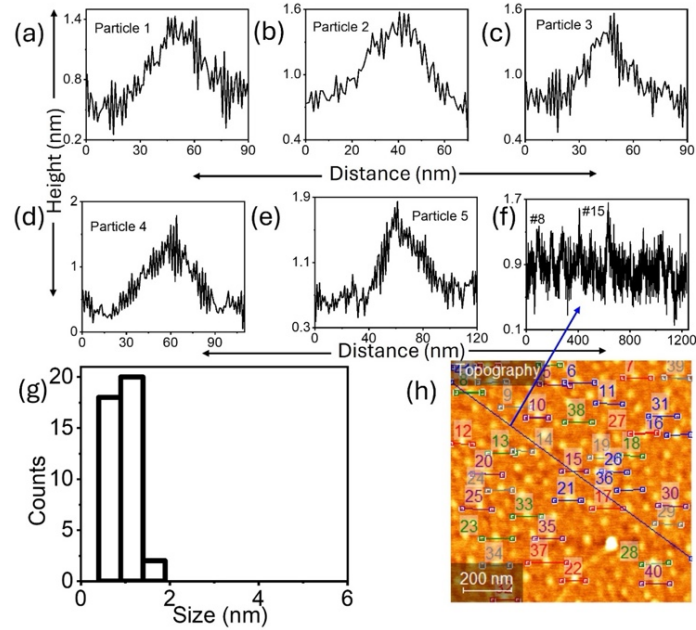


Figure S6: Particle height analyses of large NGQDs. (a-e) Height profile of selected particles, (f) line profile over the pink line indicated in (h) containing several particles out of which particle, #15 and #8 (as marked in the AFM micrograph) is indicated for easy reference, (g) histogram of height of the particles and (h) AFM image with particle numbers and lines of large NGQD.

Section 2. Tip deconvolution

The AFM tip used in this study had a radius of curvature of 67 nm. Since the average particle size measured were smaller than the tip radius, we used the following equation to correct for the tip convolution effect.¹

$$S = 2 \times \left(R \times D + \frac{D^2}{4} \right)^{1/2}$$

Section 3: Chemical analysis

Spectral Resolution

The spectral resolution is 1 wavenumber, due to a high tuneable IR laser, specifically a QCL (Quantum Cascade Laser) from Block Engineering with a spectral range of 744-1884 cm⁻¹.

The Vista One PiFM is properly calibrated with well-known IR calibration samples such as polyethersulfone (PES), polymethyl methacrylate (PMMA), Nylon and AFM calibration samples made of silicon and silicon oxide.

Table S1: Correlation table for peaks, relative intensity, and position from PiF-IR spectra of the small GQD

Particle No. Wavenumber	1	2	3	4	5	6	7	Group
1785	0	0	0	0.45	0	0	0.29	$\nu\text{C}=\text{O}^2$
1779-1778	0.4	0	0	0	0	0	0	$\nu\text{C}=\text{O}^3$
1775	0	0	0.47	0	0.12	0	0	$\nu\text{C}=\text{O}^4$
1770	0	0	0	0	0	0	0.32	$\nu\text{C}=\text{O}^4$
1765	0	0	0	0	0	0	0	$\nu\text{C}=\text{O}^5$
1760	0	0	0	0	0	0	0	$\nu\text{C}=\text{O}^6$
1755	0	0	0	0	0.13	0	0.31	$\text{C}=\text{O}^7$
1749	0.57	0.39	0.39	0	0	0	0	$\nu\text{C}=\text{O}^8$
1740	0	0	0	0	0	0	0	$\nu\text{C}=\text{O}^9$
1734- 1732	0.85	0.56	0.55	0.51	0.16	0.45	0.44	$\nu\text{C}=\text{O}^{10}$
1730	0	0	0	0	0	0	0	$\nu\text{C}=\text{O}^{11}$
1720-1718	0.57	0.41	0.45	0.5	0	0.39	0.37	$\nu\text{C}=\text{O}^{12,13}$
1700-1699	1	0.9	0.5	1	0.18	0.48	0.52	$\text{C}=\text{O}^{14}$
1690	0	0	0	0.43	0	0	0	$\text{C}=\text{O}^{15}$
1685-1680	0.77	0	0.4	0.48	0	0.35	0	$\nu\text{C}=\text{C}^{16}$
1676-1675	0	0	0	0.44	0	0	0.3	$\nu_{\text{as}}\text{HCO}_3^-$ ¹⁷
1669	0.4	0	0	0.54	0	0	0	$\nu\text{C}=\text{O}^{18}$
1654	0.62	1	1	0.64	1	1	1	$\nu\text{C}=\text{C}^6$
1640	0.64	0	0	0.47	0.13	0.29	0	$\nu\text{C}=\text{O}^{19}$
1630	0	0.42	0	0.51	0.14	0.36	0.41	$\nu\text{C}=\text{C}^{20}$
1629	0.69	0	0.52	0	0	0	0	$\nu\text{C}=\text{C}^{20}$
1625-1623	0.65	0	0	0	0	0	0	δOH^{21}
1620-1619	0.49	0	0.59	0	0	0	0	$\nu\text{C}=\text{C}^{22}$
1600	0	0	0	0	0	0.31	0.29	$\text{C}=\text{O}/\text{C}=\text{C}^{23}$
1590	0	0	0	0	0.11	0	0	$\nu\text{C}=\text{C}^{24}$
1585	0.49	0.61	0	0.58	0	0	0	$\nu\text{C}=\text{C}^{25}$
1570	0.56	0	0	0	0.14	0	0	$\nu\text{C}=\text{C}^{26}$
1565	0	0.65	0	1.44	0	0	0.26	$\nu\text{C}=\text{C}^{27}$
1560	0	0	0	0.58	0	0.34	0	$\nu\text{C}-\text{C}^{28}$
1550	0	0.4	0	0.58	0	0	0.34	$\nu\text{C}=\text{C}^{29}$
1545	0	0	0.37	0	0.14	0	0	$\nu\text{C}=\text{O}^{29}$
1540	0	0	0	0	0	0.38	0	$\text{C}=\text{C}^{30}$
1535	0	0	0	0	0	0	0.23	$\nu\text{C}=\text{C}^{31}$
1529-1528	0	0	0	0.45	0	0	0	$\nu\text{C}=\text{C}^{32}$
1510-1509	0	0.42	0	0.46	0	0	0.2	νCOO^- ³³
1505-1504	0	0	0	0	0	0	0	$\nu\text{C}=\text{O}^{34}$
1485	0	0.44	0	0.42	0	0	0	$\nu\text{C}=\text{C}^{35}$
1474	0.45	0	0	0	0	0	0	$\nu/\delta\text{CH}^{36}$
1475-1472	0	0	0	0	0	0	0.27	$\nu_{\text{s}}\text{C}-\text{O}^{37}$
1470	0	0	0	0.45	0	0	0	$\nu_{\text{sym}}\text{C}-\text{O}^{37}$
1460-1459	0	0	0.43	0	0.14	0.33	0.4	$\nu\text{C}=\text{O}^{38}$
1445	0.55	0	0	0	0.149	0	0	$\nu_{\text{sym}}\text{HCO}_3^-$ ¹⁷
1440-1439	0.53	0	0	0	0.143	0	0	δCH_3 ³⁹

1420-1419	0	0	0	0	0	0	0.28	COO ⁻ 40
1415-1414	0	0	0	0	0	0	0	ν C-H ⁴¹
1380-1379	0	0	0	0	0.149	0.34	0	CO ₃ ²⁻ 18
1374	0.53	0	0	0	0	0	0	δ OH ⁴²
1369-1368	0.421	0	0	0	0	0	0.38	β OH ⁴³
1220	0.39	0.20	0.26	0.24	0.08	0.15	0.15	COC ⁴⁴

Table S2: Correlation table for peaks, relative intensity, and position from PiF-IR of the medium GQD.

Particle No. Wavenumber	1	2	3	4	5	6	7	Group
1774	0	0	0	0	0.07	0	0.08	ν C=O ⁴⁵
1742	0	0.07	0	0	0.06	0	0.07	ν C=O ⁹
1734- 1732	0	0	0	0	0	0.11	0	ν C=O ¹⁰
1695	0.56	0.22	0.29	0.55	0.22	0.68	0.38	ν C=O ⁶
1684-1680	1	1	1	1	1	1	1	ν C=C ¹⁶
1670-1669	0.09	0	0.08	0.08	0.07	0.1	0.07	C=O ⁴⁶
1643-1641	0	0	0	0	0	0.11	0	ν CH=O ⁴⁷
1646-1645	0	0.06	0.08	0	0	0	0	HC=O ⁴⁸
1634	0	0.06	0	0.08	0	0	0	C=O-H ⁴⁹
1623-1622	0	0.07	0.07	0	0.07	0	0	δ OH ⁵⁰
1594	0	0	0	0	0.06	0	0	C=C ⁵¹
1564	0	0	0	0	0.06	0	0	ν C=C ⁵²
1547	0	0	0	0	0.07	0	0	ν C=C ⁵³
1509	0	0	0	0	0.05	0	0	ν COO ⁻ 33
1472	0	0.06	0	0.07	0.06	0.11	0	ν_s C-O ³⁷
1459	0	0	0	0	0	0.12	0	ν C=C ⁵⁴
1456-1455	0	0	0.07	0.08	0.08	0	0.06	OH ⁵⁵
1441-1440	0	0	0	0	0	0	0.06	δ CH ⁵⁶
1423	0	0	0	0	0	0	0.06	δ OH ⁵⁷
1420	0	0	0	0.07	0.06	0.12	0	COO ⁻ 40
1398	0	0	0	0	0	0	0.06	ν C=C ⁵⁴
1369-1368	0	0	0	0	0.06	0	0	β OH ⁴³
1375	0	0	0	0.06	0	0	0	OCHO ⁵⁸
1361	0	0	0	0	0	0	0.05	ν C-O ⁵⁹
1338	0.06	0	0	0	0	0	0	δ/ν OH ⁶⁰
1337-1336	0	0	0	0	0	0.06	0	CH ₃ CH ₂ O ⁶¹
1284	0	0	0	0	0.04	0	0	ν C-O Aromatic ⁶²
1262-1260	0	0	0.06	0.06	0	0.09	0.07	ν C-O ⁶³
1258-1256	0.08	0.44	0	0	0	0	0	ν_{as} COC ^{64,65}
1254	0	0	0	0	0.05	0	0	ν C-O ⁶⁶

Table S3: Correlation table for peaks, relative intensity, and position from PiF-IR of the large GQD.

Particle No. Wavenumber	1	2	3	4	5	6	7	Group
1778	0.06	0	0	0	0	0	0	ν C=O ³
1760-1759	0.08	0	0	0	0	0	0	ν C=O ⁶
1742	0.09	0.1	0.09	0.13	0.09	0.11	0.11	ν C=O ⁹

1734	0	0.06	0.07	0.08	0	0	0	$\nu\text{C}=\text{O}^{10}$
1710	0	0.06	0.07	0.1	0	0	0	COOH^{67}
1695	0.23	0.22	0.27	0.35	0.25	0.28	0.23	$\nu\text{C}=\text{O}^6$
1684-1680	1	1	1	1	1	1	1	$\nu\text{C}=\text{C}^{16,46}$
1669	0.08	0.09	0.08	0.11	0.09	0.1	0.09	$\text{C}=\text{O}^{68}$
1643	0	0.07	0	0	0	0	0	$\nu\text{CH}=\text{O}^{47}$
1638	0.08	0	0	0	0	0	0	$\nu\text{C}=\text{C}^{49}$
1634	0	0	0.08	0	0.08	0	0	$\text{C}=\text{O}-\text{H}^{49}$
1585	0	0	0	0	0	0.07	0	$\nu\text{C}=\text{C}^{25}$
1557	0	0	0	0	0.06	0	0	νCH^{69}
1568	0.06	0	0	0	0	0	0	νCOOH^{61}
1528	0	0	0	0	0	0	0.05	$\nu\text{C}=\text{C}^{32}$
1496	0	0	0	0	0	0.06	0	$\text{OC}-\text{CO}^{17}$
1472	0	0.05	0	0.06	0.05	0	0	$\nu_s\text{C}-\text{O}^{37}$
1456	0.07	0.06	0	0.08	0	0.06	0.06	OH^{55}
1420-1419	0.06	0	0	0.08	0.06	0.06	0.07	COO^{-40}
1398	0	0.06	0.07	0	0	0	0.06	$\nu\text{C}=\text{C}^{54}$
1395	0.05	0	0	0.05	0	0	0	$\text{O}=\text{C}-\text{O}/\delta(\text{C}-\text{C})^{17,70}$
1390	0	0	0	0	0	0.06	0	νOH^{71}
1368	0.05	0	0	0	0	0	0	βOH^{43}
1323	0	0	0	0.05	0.03	0	0	$\nu(\text{C}-\text{C})^{72}$
1258-1256	0.06	0.06	0	0	0.05	0	0	COC^{64}
1253-1249	0	0	0.05	0.08	0	0.05	0.05	$\nu\text{C}-\text{O}^{73}$

Table S4: Correlation table for peaks, relative intensity, and position from PiF-IR of the small NGQD.

Particle No. Wavenumber	1	2	3	4	5	6	7	Group
1773	0	0.04	0	0.08	0.05	0.06	0.09	$\nu\text{C}=\text{O}^{74}$
1734	0.088	0.04	0.07	0.08	0.06	0.1	0.12	$\nu\text{C}=\text{O}^{10}$
1718	0.099	0.09	0.09	0.08	0.06	0.09	0.18	$\nu\text{C}=\text{O}^{13}$
1700	0.33	0.27	0.26	0.27	0.31	0.27	0.65	$\text{C}=\text{O}^{75}$
1685	0.23	0.16	0.2	0.27	0.17	0.28	0.3	$\nu\text{C}=\text{O}/\nu\text{C}=\text{C}^{16,76}$
1653	1	1	1	1	1	1	1	$\nu\text{C}=\text{C}^{6,77}$
1647	0.16	0	0	0	0	0	0	$\nu\text{C}=\text{O}^{77,78}$
1636	0.19	0.13	0.15	0.2	0.15	0.18	0.27	$\nu\text{C}=\text{O}/\nu\text{C}=\text{C}^{21,49,79}$
1623	0.21	0	0.16	0.25	0.15	0.2	0.33	δOH^{21}
1570-1560	0	0.1	0	0.17	0.12	0.13	0.19	$\delta\text{N}-\text{H}$ & $\nu\text{C}-\text{N}^{80}$
1541-1540	0.16	0.1	0.12	0	0.11	0.16	0.27	νNH & $\text{CN}/\nu\text{C}-\text{C}^{81,82}$
1473	0.16	0.09	0.11	0.16	0.13	0.14	0.21	CH_3^{83}
1450	0	0.09	0	0.16	0	0	0	$\text{C}-\text{O}^{80}$
1437	0	0.1	0.11	0	0	0	0.24	$\delta\text{CH}_3/\nu_{\text{as}}\text{O}-\text{C}-\text{O}^{39,84}$
1420	0.18	0.12	0.14	0.23	0.14	0.19	0.22	COO^{-40}
1354	0.18	0.11	0.1	0.19	0.15	0.15	0.23	$\text{C}=\text{N}/\text{phenazine}^{85}$
1244	0.05	0.04	0.05	0.06	0.05	0.06	0.1	$\text{C}=\text{O}^{86}$

Table S5: Correlation table for peaks, relative intensity, and position from PiF-IR of the medium NGQD.

Particle No. Wavenumber	1	2	3	4	5	6	7	Group
1778	0	0	0	0.09	0	0	0.11	$\nu\text{C}=\text{O}^3$
1770	0	0	0	0.09	0	0.13	0	$\nu\text{C}=\text{O}^{87}$
1755	0	0	0.11	0	0	0	0	$\text{C}=\text{O}^7$
1742	0.15	0.2	0.17	0.17	0.19	0.22	0.18	$\nu\text{C}=\text{O}^9$
1734	0	0	0.11	0.12	0	0	0	$\nu\text{C}=\text{O}^{10}$
1695	0.35	0.4	0.34	0.36	0.33	0.45	0.34	$\nu\text{C}=\text{O}^6$
1684	1	1	1	1	1	1	1	$\nu\text{C}=\text{C}^{16,46}$
1669	0.13	0.13	0.15	0.11	0.12	0.14	0.14	$\nu\text{C}=\text{O}^{18}$
1660	0	0	0.17	0	0	0	0	$\nu\text{C}=\text{O}$ & $\beta\text{N}-\text{H}^{88}$
1649	0.12	0	0.08	0.1	0.12	0.13	0	$\nu\text{C}=\text{C}^9$
1643	0	0	0	0	0	0	0.12	$\nu\text{C}=\text{O}^{47}$
1629-1624	0	0.13	0	0.11	0.12	0.14	0.12	$\nu\text{C}=\text{O}^{29}$
1591-1588	0	0.09	0	0.08	0.1	0	0.09	δNH_3^{89}
1585	0.08	0	0	0	0	0	0	$\nu\text{C}=\text{C}^{25}$
1574-1572	0.08	0	0	0	0.11	0	0	$\nu\text{C}-\text{N}^{15}$
1570-1567	0	0	0	0	0	0	0.09	$\delta\text{N}-\text{H}$ & $\nu\text{C}-\text{N}^{80}$
1554	0	0	0	0	0	0.1	0	$\text{C}=\text{C}^{79}$
1547-1545	0	0.11	0	0	0.09	0	0	$\nu\text{CN}+\delta\text{CHN}/$ $\text{C}=\text{N}^{29,46}$
1536	0	0	0	0	0	0.09	0	δNH & νCN^{90}
1514	0	0	0	0	0	0	0.07	$\nu\text{C}-\text{O}^{62}$
1509	0	0	0	0	0	0.09	0	NH_2^{91}
1490	0.06	0	0	0	0	0	0	$\nu\text{C}=\text{N}^{92}$
1472	0.08	0	0	0	0.09	0.1	0.09	$\nu_s\text{C}-\text{O}^{37}$
1456	0.1	0.13	0.11	0.1	0.12	0.14	0.12	$\text{C}-\text{N}/\text{C}=\text{N}^6$
1446	0	0	0	0	0	0.1	0	$\nu_a(\text{C}=\text{N})^{18}$
1439	0	0	0	0	0.1	0	0	δCH_3^{39}
1419	0.08	0.09	0.09	0.08	0.09	0	0.1	COO^{40}
1395	0	0.09	0.07	0.08	0.1	0	0.09	$\text{O}=\text{C}-\text{O}-/\delta\text{C}-$ $\text{C}^{17,70}$
1372	0	0	0.06	0	0.08	0	0.07	$\text{OC}-\text{CO}^{17}$
1337	0.04	0	0	0	0	0	0	$\text{CH}_3\text{CH}_2\text{O}^{61}$
1332	0	0	0	0	0.05	0.06	0	
1301	0	0	0.05	0	0	0	0	$\text{C}-\text{N}$ secondary aromatic amine ⁹²
1293	0	0	0	0	0	0.06	0	$\nu\text{C}=\text{O}^{93}$
1251	0.06	0.09	0.09	0.09	0.08	0.09	0.08	$\nu\text{C}-\text{O}^{73}$

Table S6: Correlation table for peaks, relative intensity, and position from PiF-IR of the large NGQD.

Particle No. Wavenumber	1	2	3	4	5	6	7	Group
1779-1778	0.06	0	0	0	0	0	0.06	$\nu\text{C}=\text{O}^3$
1763	0.06	0	0	0	0	0	0	$\nu\text{C}=\text{O}^{94}$
1760	0	0	0	0	0	0	0.06	$\nu\text{C}=\text{O}^6$
1747	0.06	0	0	0	0.16	0	0	$\nu\text{C}=\text{O}/\text{COOH}^{60}$
1734	0.059	0.2	0	0	0	0.08	0.06	$\nu\text{C}=\text{O}^{10}$
1718	0	0.15	0.13	0.27	0	0	0.06	$\nu\text{C}=\text{O}^{13}$
1701-1700	0.06	0.25	0.3	0.41	0.35	0.11	0	$\text{C}=\text{O}^{75}$
1685	0	0.23	0.13	0.42	0.31	0.11	0.1	$\nu\text{C}=\text{C}/\nu\text{C}=\text{O}^{16,76}$
1676	0.08	0	0	0	0	0.09	0	$\nu_{\text{as}}\text{HCO}_3^{-17}$
1669	0	0	0	0	0.11	0	0	$\text{C}=\text{O}^{68}$
1663	0	0	0.13	0.26	0	0	0.07	$\text{C}=\text{O}^{95}$
1653	1	1	1	1	1	1	1	$\nu\text{C}=\text{C}^6$
1635	0	0	0.08	0	0	0	0.06	$\nu\text{C}=\text{O}^{49,79}$
1625-1623	0	0	0	0	0.11	0.04	0	δOH^{21}
1602	0	0.13	0	0	0	0	0	$\text{oC}-\text{N}^{96}$
1598	0	0	0	0	0.09	0	0	$\nu\text{C}=\text{C}^{97}$
1570-1567	0	0	0	0.13	0	0	0	$\delta\text{N}-\text{H} \ \& \ \nu\text{C}-\text{N}^{80}$
1560-1559	0.05	0.11	0.15	0.14	0	0.05	0.07	$\delta\text{N}-\text{H} \ \& \ \nu\text{C}-\text{N}^{80}$
1558	0	0	0	0	0.14	0	0	$\nu\text{C}-\text{N}^{98}$
1544	0	0.11	0	0	0	0	0	$\nu\text{CN}+\delta\text{CHN}^{46}$
1541	0.048	0	0	0.18	0	0	0	$\nu\text{C}-\text{C}^{82}$
1536-1534	0	0	0.07	0	0	0	0	$\delta\text{NH} \ \& \ \nu\text{C}-\text{N}^{90}$
1511	0.05	0	0	0	0	0	0	COOH^{99}
1509-1507	0	0	0.07	0.18	0.15	0	0	$\text{NH}_2/\nu_{\text{as}}\text{COOH}^{33,91}$
1472	0	0	0	0	0.13	0.05	0	$\nu_{\text{s}}\text{C}-\text{O}^{37}$
1459-1456	0.06	0	0.08	0.16	0	0.05	0.07	$\text{C}-\text{N}/\text{C}=\text{N}^6$
1438-1437	0	0	0	0.22	0	0.06	0	δCH_3^{39}
1420-1419	0	0	0	0	0.11	0.05	0	COO^{-40}
1396	0	0	0.08	0	0	0	0	COH^{100}
1386	0.052	0	0	0	0	0	0	$\text{C}-\text{N}^{101}$
1354-1349	0.09	0.17	0.13	0.21	0.22	0.1	0.07	$\text{C}=\text{N}/\text{phenazine}^{85}$
1338	0.05	0	0	0	0	0	0	$\delta/\nu\text{OH}^{60}$
1312	0.04	0	0	0	0	0	0	$\delta/\nu\text{C}-\text{N}^{102}$
1307	0	0	0	0.12	0	0	0	$\text{C}-\text{N}^{103}$
1305	0	0	0	0	0	0.04	0	NH_4^{+104}
1295	0	0	0	0	0	0	0.04	$\nu\text{C}-\text{O}^{105}$
1259-1245	0.04	0	0.08	0	0.15	0	0	$\nu_{\text{as}}\text{COC}/\text{C}-\text{N}^{35,65}$
1228	0	0.14	0	0	0	0	0	$\text{N}_{\text{as}}\text{COC}^{106}$

Table S7: Statistical analysis of spectral variability across the 94 GQD particles

Peak (cm^{-1})	Mean (cm^{-1})	Standard Deviation (cm^{-1})
1217-1223	1219.8	1.2

1252-1257	1253.8	1.0
1442-1447	1444.6	1.1
1457-1462	1459.8	1.0
1650-1658	1654.2	1.4
1682-1686	1684.1	0.7
1697.5-1701.5	1699.8	0.9
1717-1722	1719.4	1.0
1740-1744	1741.5	0.7

Table S8: Statistical analysis of intensity variability across 94 GQD particles

Peak (cm ⁻¹)	Mean Intensity (a.u.)	Standard Deviation Intensity (a.u.)
1220	8.46922E-6	5.99941E-6
1253	1.31354E-5	5.4036E-6
1445	1.72156E-5	1.09866E-5
1460	1.98768E-5	1.59078E-5
1654	2.32108E-5	2.02646E-5
1685	1.30733E-4	9.71286E-5
1700	3.27514E-5	1.62827E-5
1720	2.38648E-5	1.96598E-5
1742	2.30944E-5	8.66496E-6

Table S9: Statistical analysis of spectral variability across the 78 N-GQD particles

Peak (cm ⁻¹)	Mean (cm ⁻¹)	Standard Deviation (cm ⁻¹)
1353-1356	1353.9	0.7
1419-1421	1419.8	0.5

1506-1510	1507.9	1.0
1539-1543	1540.6	0.7
1558-1562	1559.6	0.9
1621-1628	1622.8	0.9
1651-1658	1653.4	1.0
1674-1678	1675.9	0.6
1683-1686	1684.7	0.43
1692-1698	1695.3	0.8
1697-1702	1699	0.5

Table S10: Statistical analysis of intensity variability across 78 GQD particles

Peak (cm⁻¹)	Mean Intensity (a.u.)	Standard Deviation Intensity (a.u.)
1354	3.69281E-4	0.00259
1420	8.62776E-4	0.00703
1509	6.63215E-4	0.00551
1540	7.36637E-4	0.00603
1560	8.65876E-4	0.00722
1623	0.00118	0.00983
1653	0.00146	0.008
1676	0.00101	0.00846
1685	0.00301	0.02546
1696	0.00187	0.01612
1700	0.00175	0.01517

No	DFT predicted IR peak (cm ⁻¹)	IR peak position measured by PiF-IR (cm ⁻¹)	Group	Difference with respect to DFT (cm ⁻¹)	References
1.	1745	1750-1742	$\nu\text{C=O}$	-3 to +5	9,60
2.	1732	1735-1732	$\nu\text{C=O}$	0 to +3	10
3.	1695	1693	$\nu\text{C=O}$	-2	6
4.	1682	1684	$\nu\text{C=C}$	+2	16
5.	1664	1669	$\nu\text{C=O}$	+5	18
6.	1645	1653	$\nu\text{C=C}$	+8	6
7.	1617-1609	1613	CH	-4 to +4	46
8.	1575	1573	CH	-2	46
9.	1528	1524	C=C	-4	32
10.	1418	1420	C=O	-2	40
11.	1376-1351	1375	OCHO	-1 to 24	58
12.	1266	1261	C-O	-5	20

Table S11: Comparison of IR spectra from DFT and PiF-IR of GQD

Table S12: Comparison of IR spectra from DFT and PiF-IR of NGQD

No	DFT predicted IR peak (cm ⁻¹)	IR peak position measured by PiF-IR (cm ⁻¹)	Group	Difference with respect to DFT (cm ⁻¹)	References
1.	1745	1747	$\nu\text{C=O}$	+2	9
2.	1736	1739-1734	$\nu\text{C=O}$	-3 to +2	10
3.	1720	1718	$\nu\text{C=O}$	-2	13
4.	1701	1700	$\nu\text{C=O}$	-1	75
5.	1680	1684-1675	$\nu\text{C=C}$	-4 to +5	16
6.	1662	1659	$\nu\text{C=O}$ & $\beta\text{N-H}$	+3	88
7.	1653	1650	$\nu\text{C=C}$	-3	6
8.	1637-1623	1635-1623	$\nu\text{C=O}$	0 to +2	49
9.	1565	1559	$\delta\text{N-H}$ & $\nu\text{C-N}$	+7	80
10.	1508	1509	$\text{NH}_2/\nu_{\text{as}}\text{COOH}$	-1	33,91
11.	1476	1472	$\nu_{\text{s}}\text{C-O}$	+4	37
12.	1433	1437	δCH_3	-4	39
13.	1420	1420	C=O	0	40
14.	1364-1346	1354	Phenazine	-4 to +10	85
15.	1249	1244	$\nu_{\text{as}}\text{COC/C-N}$	-5	35

Section 4: Optical Properties

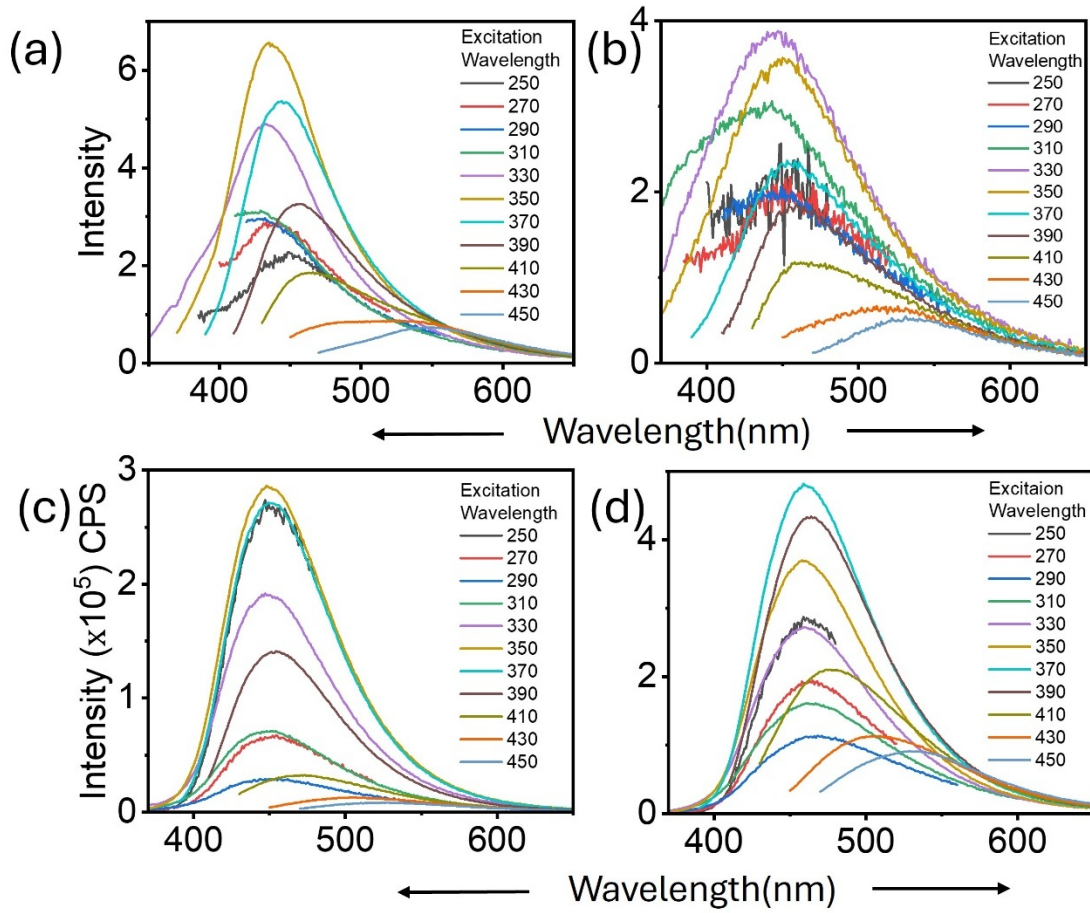


Figure S7: Normalized Emission at different excitation wavelength of (a) small, (b) medium GQDs and (c) Medium (d) Large NGQDs.

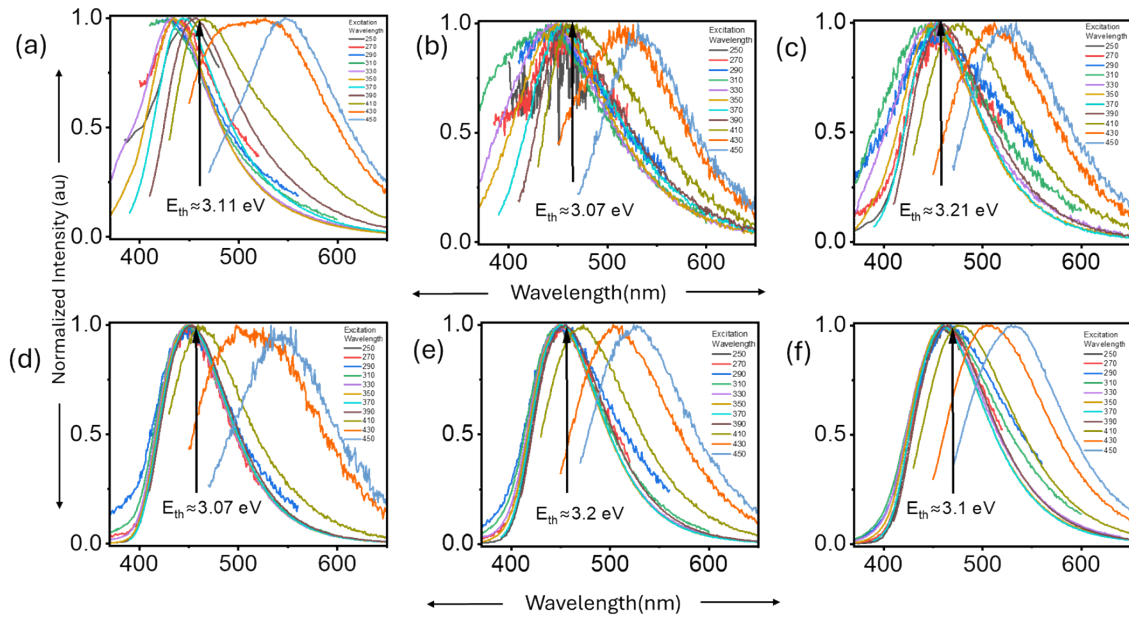


Figure S8: Normalized Emission at different excitation wavelength of (a) small, (b) medium, (c) large GQDs, and (d) small, (e) medium, (f) large NGQDs.

Table S13: Value of E_{th}

$E_{th}(eV)$	Large	Medium	Small
GQD	3.21	3.07	3.11
NGQD	3.1	3.2	3.07

Table S14: Parameters for exponential fit of time resolved photoluminescence spectra of GQDs

Large	Medium	Small
$R_1^2=0.99$	$R_2^2=0.99$	$R_3^2=0.99$
$\alpha_{11}=250$	$\alpha_{21}=546$	$\alpha_{31}=650$
$\alpha_{12}=749$	$\alpha_{22}=400$	$\alpha_{32}=354$
$\tau_{11}=3.4$	$\tau_{21}=3.9$	$\tau_{31}=3.4$
$\tau_{12}=12.5$	$\tau_{22}=11.4$	$\tau_{32}=11.2$
$\tau_{1avg}=12.5$	$\tau_{2avg}=9.03$	$\tau_{3avg}=8.4$

Table S15: Parameters for exponential fit of time resolved photoluminescence spectra of NGQDs

Large	Medium	Small
$R_3^2=0.99$	$R_2^2=0.99$	$R_1^2=0.99$
$\alpha_{11}=4266$	$\alpha_{21}=623$	$\alpha_{31}=1583$
$\alpha_{12}=1228$	$\alpha_{22}=1717$	$\alpha_{32}=481$
$\tau_{11}=4.3$	$\tau_{21}=5.6$	$\tau_{31}=13.1$
$\tau_{12}=14.8$	$\tau_{22}=15.8$	$\tau_{32}=20.3$
$\tau_{1avg}=9.5$	$\tau_{2avg}=14.7$	$\tau_{3avg}=15.4$

Section 5. Stability

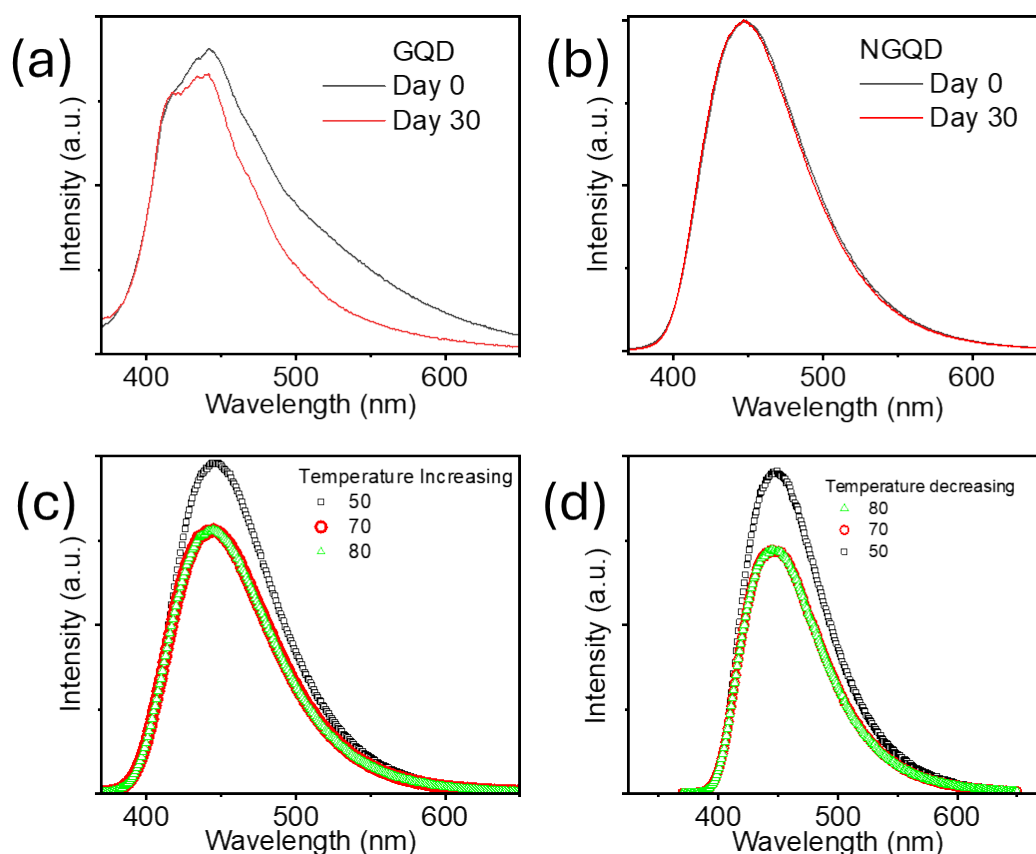


Figure S9: (a) Comparison of PL spectra of GQD one month apart. (b) Comparison of PL spectra of N-GQD one month apart. (c) Comparison of PL spectra of NGQD at increasing temperature. (d) Comparison of PL spectra of NGQD at decreasing temperature.

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