

Supporting Information for

An efficient Edge-Functionalization Method to Tune the Photoluminescence of Graphene Quantum Dots

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Experimental

Preparation of GQDs: Graphene sheets (10 mg, from Nanjing XFNANO Materials Tech Co., Ltd) were oxidized in piranha solution ($V_{\text{H}_2\text{SO}_4} : V_{\text{H}_2\text{O}_2} = 7 : 3$) at 80°C for 30 min (*Caution:* piranha solution is highly corrosive). Then the mixture was diluted with deionized (DI) water (250 mL) and the pH was adjusted to neutrality with sodium hydroxide in the ice-water bath. After that, the colloidal solution was dialyzed in a dialysis bag (1000 molar mass cutoff) for 5 days to remove the salt. After concentration, the strongly fluorescent part with nominal molecular weight of < 3 kDa was obtained via ultrafilter. Finally, the GQDs powders were obtained through freeze drying (yield of ca. 8%).

Fabrication of the modified GQDs: For the preparation of BDA-GQDs, the resulting homogeneous GQDs water dispersion 1 mL (1.35 mg mL^{-1}) was mixed with 5.0 μL of hydrochloric acid solution (37 wt% in water) and 5 mL of deionized water in a three-necked flask. In an argon atmosphere, BDA (1 mg) dissolved in 3 mL of the deionized water was slowly added to the reaction mixture, which was heated at 40°C with stirring overnight. Then, 40 μL of hydrochloric acid solution was added to turn the redundant BDA into ammonium salt and the final solution was dialyzed in a dialysis bag (1000 molar mass cutoff) for three days. After concentration, the BDA-GQDs were obtained.

For the preparation of EDA-GQDs, EDA (100 μL) was added in 1 mL water containing GQDs (1.35 mg mL^{-1}) and the similar procedures for BDA-GQDs were carried out.

For the preparation of NDA-GQDs, NDA (1.5 mg) was dissolved in ethanol/water (2 mL, volume ratio=1:1) and the acid-catalyzed dehydration reactions processed in

ethanol/water (volume ratio=1:1) mixing system. Other reaction conditions were the same as the fabrication of BDA-GQDs. After the ethanol was removed by rotary evaporation, 40 μL of hydrochloric acid solution was added. Then, the extraction system composed of ethyl acetate/water (volume ratio=1:1) were used to wash the NDA-GQDs three times. The resulting NDA-GQDs were dispersed in ethanol.

Preparation of D-GQDs: D-GQDs powders were obtained by thermal deoxidization of GQDs powders in a muffle furnace at 450°C for 2 h with a heating rate of 5°C min⁻¹ in a hydrogen atmosphere.

Characterization: AFM images were taken using a SPM-9500J3 atomic force microscope by the tapping mode on the mica substrate. Fluorescence spectra were recorded on a Horiba Jobin Yvon Fluorolog-3 fluorescence spectrometer. HR-TEM images were performed on a JEOL JEM-2100F high-resolution field-emission transmission electron microscope. FTIR spectra were obtained on a Thermo Nicolet 360 FT-I spectrophotometer. XPS spectra were collected using a VG Multilab 2000 X-ray photoelectron spectrometer. CV measurements were carried out on a CHI 660C electrochemical analyzer (Shanghai CH Instrument Company, China) at room temperature using a three-electrode system consisted of a platinum wire as the auxiliary electrode, a Ag/AgCl electrode as the reference electrode, and a glass carbon electrode (GCE, 3 mm in diameter) as the working electrode.

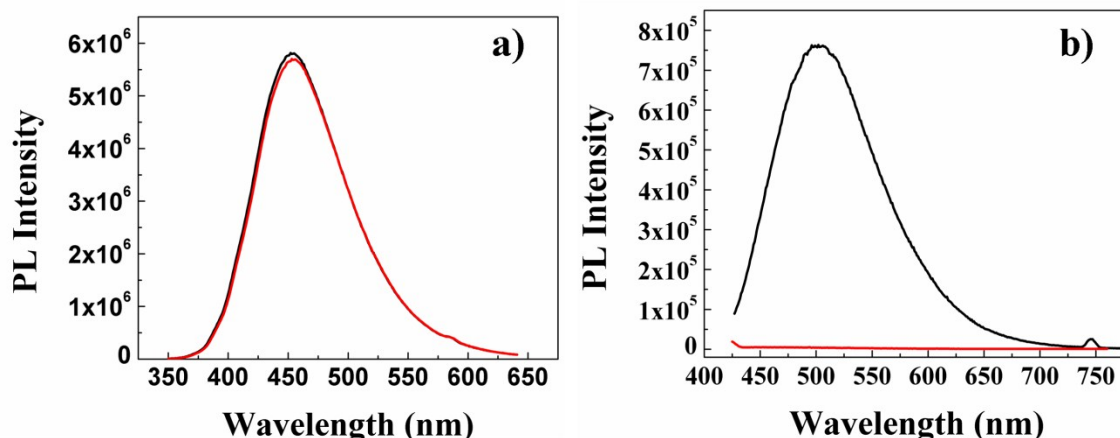


Figure S1. (a) The controlled experiments of PL spectra of aqueous GQDs before (black line) and after the acid-catalyzed reactions without 1,2-diamine compounds (red line). (b) The controlled experiment of PL spectra of aqueous BDA-GQDs (black line) and BDA after the acid-catalyzed reactions without GQDs (red line).

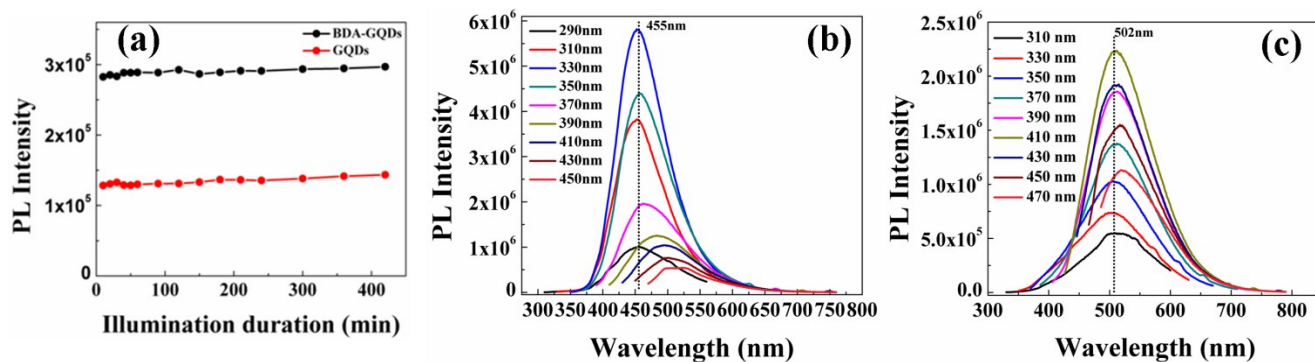


Figure S2. (a) Dependence of PL intensity on excitation time for GQDs and BDA-GQDs dispersed in water, showing the stable PL emissions. PL emission spectra of GQDs (b) and BDA-GQDs (c) dispersed in water. The excitation wavelengths varied from 290 to 450 nm with 20 nm increments as indicated.

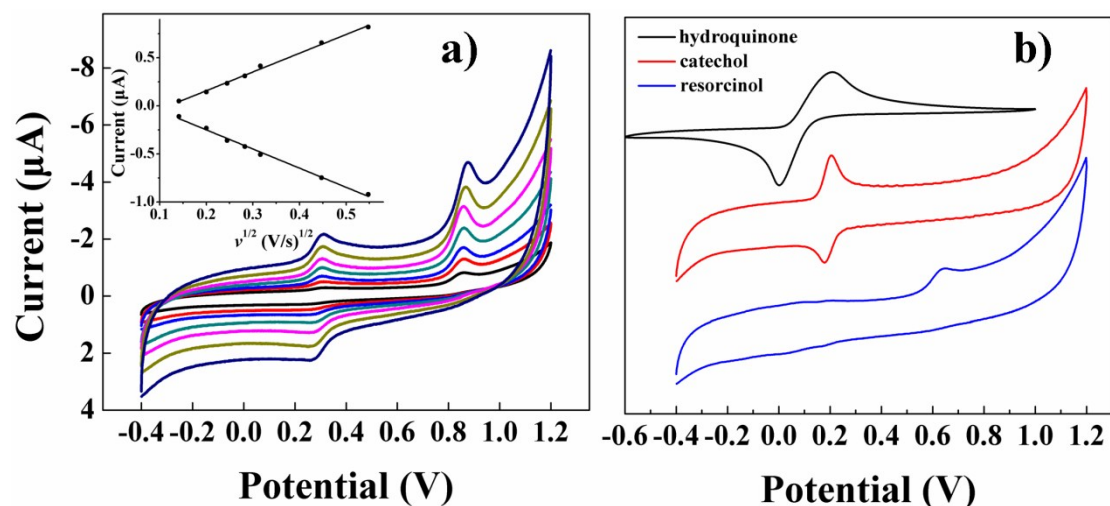


Figure S3. (a) The reduction and the oxidation peak currents of GQDs exhibited a linear relationship with the square root of the scan rate in the range from 0.02 V/s to 0.3 V/s, indicating that the redox processes were diffusion-controlled in the selected scan rate range. The redox peak currents followed the linear regression equation of $I_{pa} = -5.1006 v^{1/2} + 0.3983$ ($R = 0.994$) and $I_{pc} = 4.9945 v^{1/2} - 0.5953$ ($R = 0.995$). (b) CVs of the GCE in 0.2 M pH 7.2 PBS with hydroquinone, catechol and resorcinol at 0.1 V/s.

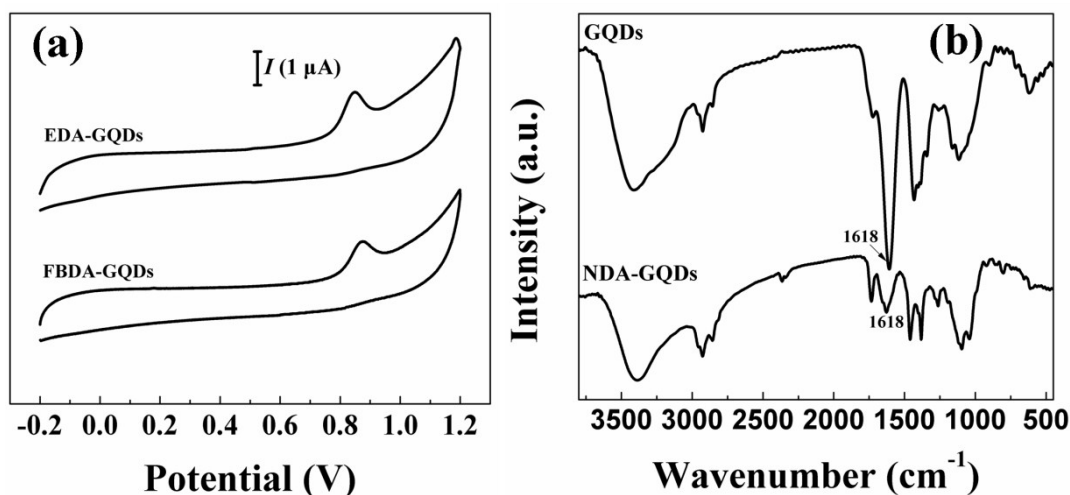


Figure S4. (a) CVs of the GCE in 0.2 M pH 7.2 PBS containing EDA-GQDs or FBDA-GQDs. (b) FTIR spectra of GQDs and NDA-GQDs. For the poor water-solubility of NDA-GQDs, FTIR was adopted to testify that GQDs were successfully modified with NDA. The stretching vibration ($\text{C}=\text{O}$ 1618 cm^{-1}) of NDA-GQDs was sharply weakened compared to that of GQDs, indicating GQDs were efficiently reacted with the NDA.

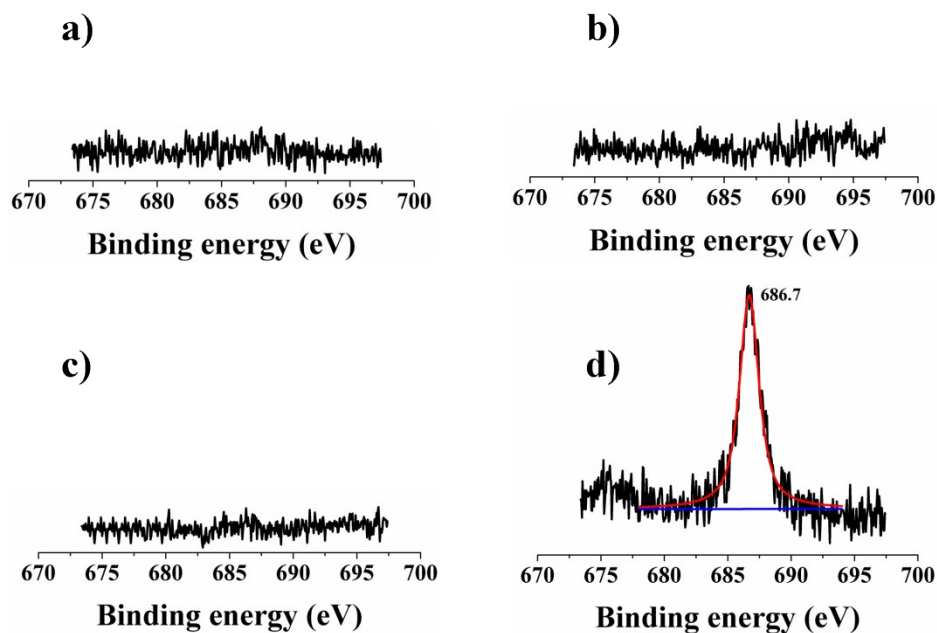


Figure S5. High-resolution XPS spectra of F 1s peaks: (a) graphene, (b) GQDs, (c) BDA-GQDs and (d) FBDA-GQDs.

Table S1. Relative content of carbon, nitrogen and oxygen (calculated by integrating fitting curve area of C 1s, N 1s and O 1s XPS).

Samples	C (area %)	N (area %)	O (area %)	oxygen-to-carbon ratio
GQDs	63.94	1.23	34.83	0.55
EDA-GQDs	63.45	2.98	33.57	0.53
BDA-GQDs	64.06	3.24	32.70	0.51
NDA-GQDs	64.54	3.31	32.15	0.50
D-GQDs	70.37	0.98	28.65	0.41

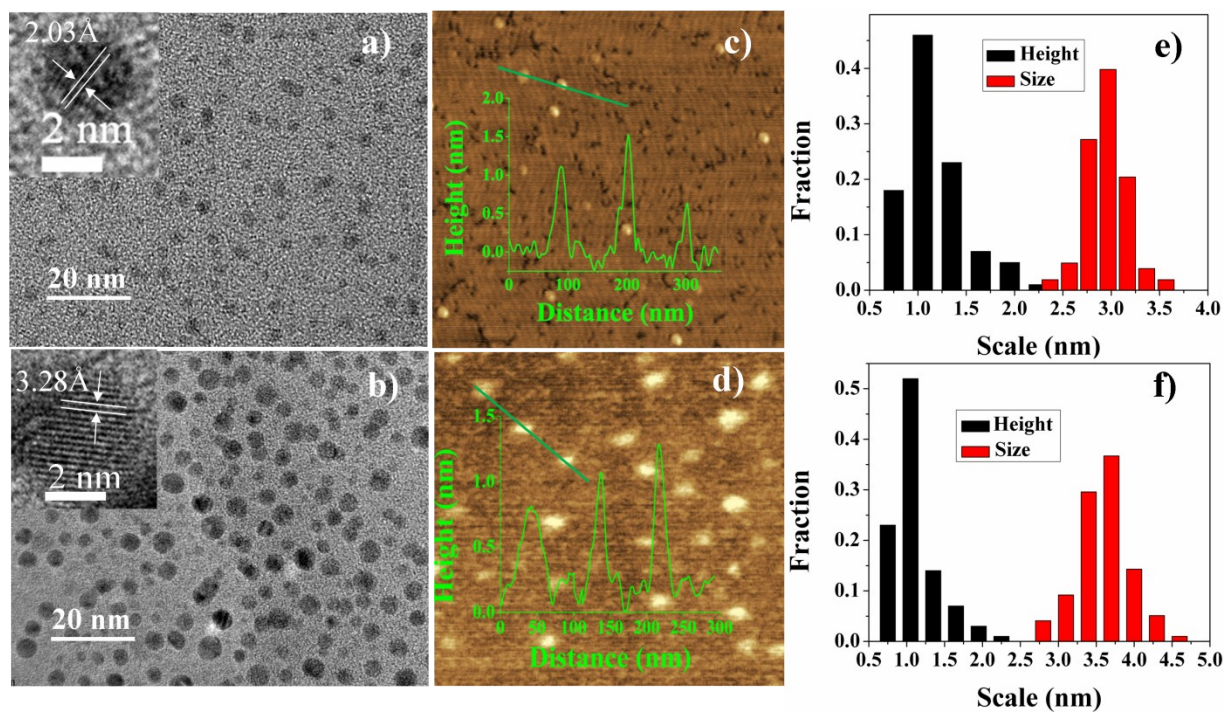


Figure S6. HRTEM images of EDA-GQDs (a) and NDA-GQDs (b). The inset of (a) and (b) is a representative image of individual EDA-GQDs and NDA-GQDs, respectively. AFM images and their corresponding height profiles of EDA-GQDs (c) and NDA-GQDs (d). The corresponding size and height distributions of EDA-GQDs (e) and NDA-GQDs (f).

Calculations

Electronic structure calculations were carried out using density functional theory (DFT) as implemented in the DMol³ program^[1]. The local density approximation (LDA) functionals with the all-electrons double-zeta numerical basis set plus *d* polarizations (DND) were employed to optimize the geometrical parameters of the GQDs. Subsequently, the band-gap energies were calculated using the time-dependent (TD) DFT as implemented in the Gaussian09 program (Revision C.01, Gaussian, Inc., Wallingford, CT, 2009). Handy's' long-range corrected version of B3LYP with the coulomb-attenuating method, namely, CAM-B3LYP^[2], was utilized with the 6-31G(d) basis set. Solvent (ethanol) effect was considered using the polarizable continuum model with the integral equation formalism (IEFPCM)^[3].

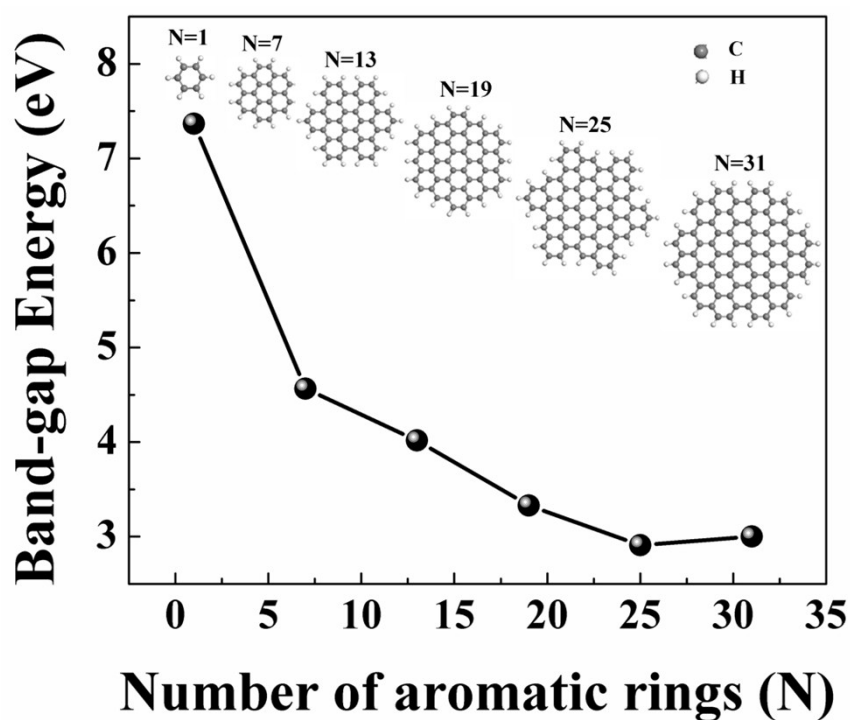


Figure S7. Convergence of the calculated band-gap energies for various sizes of the aromatic rings (N) dispersed in ethanol. The inset shows the structures of the graphene molecules used in the calculations.

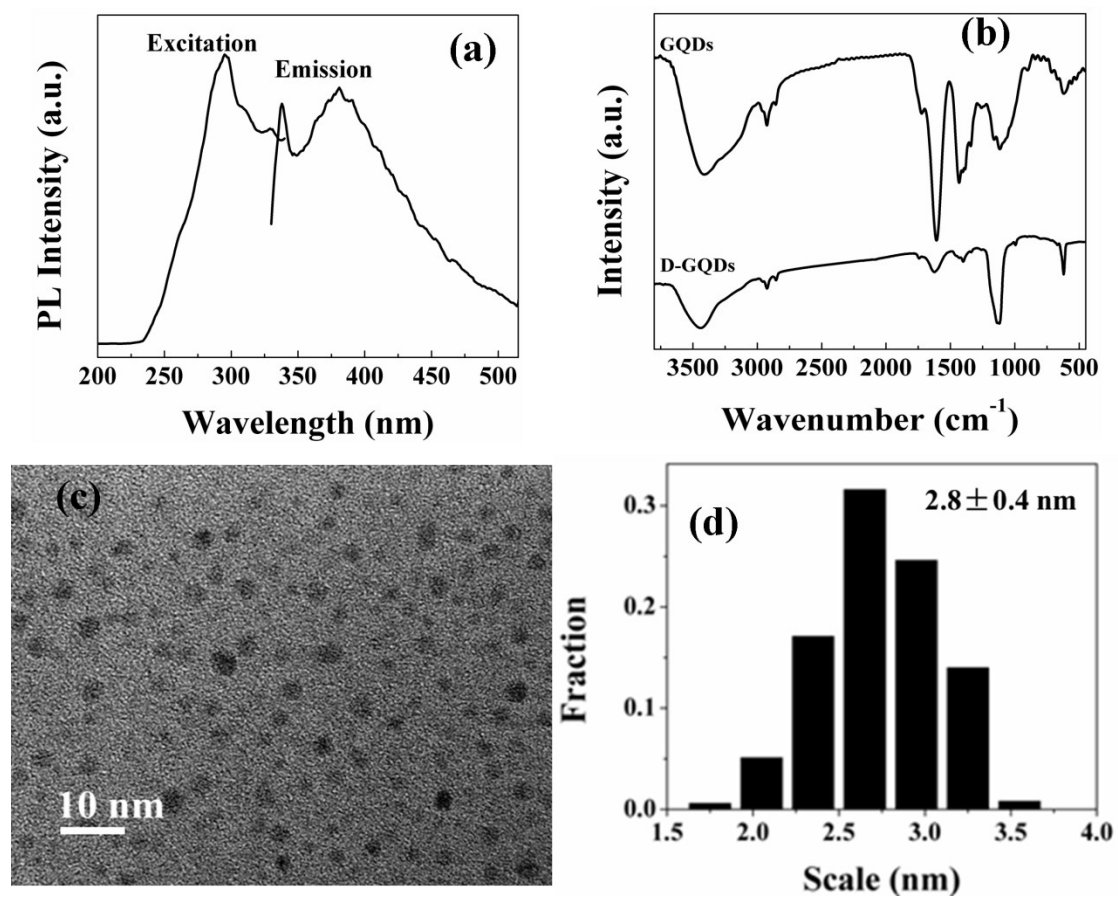


Figure S8. (a) PL excitation and emission spectrum of the deoxidized GQDs (D-GQDs) dispersed in ethanol. (b) FTIR spectra of GQDs and D-GQDs. HRTEM images of D-GQDs (c) and the corresponding size distributions (d).

Quantum yield measurements

The quantum yields of GQDs were measured on a Horiba Jobin Yvon Fluorolog-3 fluorescence spectrometer. Quinine sulfate (QS) dissolved in 0.1 M H₂SO₄ was used as the reference standard (quantum yield = 54%). The relative quantum yields of GQDs were calculated from the following equation:

$$\Phi_x = \Phi_{ST} (m_x / m_{ST}) (\eta_x / \eta_{ST})^2 \quad (1)$$

where the subscripts *ST* and *X* denote the standard and tested sample, respectively, Φ is the fluorescence quantum yield, *m* is the slope from the plot of the integrated fluorescence intensity vs. the absorbance of the sample or the standard at different concentrations, and η is the refractive index of the solvent.

The detailed procedure was as follows: (1) Measure the integrated PL intensities (excited at 360 nm) and the absorbance (less than 0.1) at 360 nm of QS at different concentrations. (2) Plot the integrated PL intensity vs. the absorbance of QS, which should be a straight line with a slope (*m*_{ST}) (Figure S10b). (3) Measure the integrated PL intensities (excited at 360 nm) and the absorbance (less than 0.1) at 360 nm of a GQDs sample at different concentrations. (4) Plot the integrated PL intensity vs. the absorbance of the GQDs sample, obtaining a slope (*m*_x) (Figure S10a). (4) Calculate the relative quantum yield of the GQDs samples according to Equation (1) and the value of quantum yields of GQDs were listed in the Table S2.

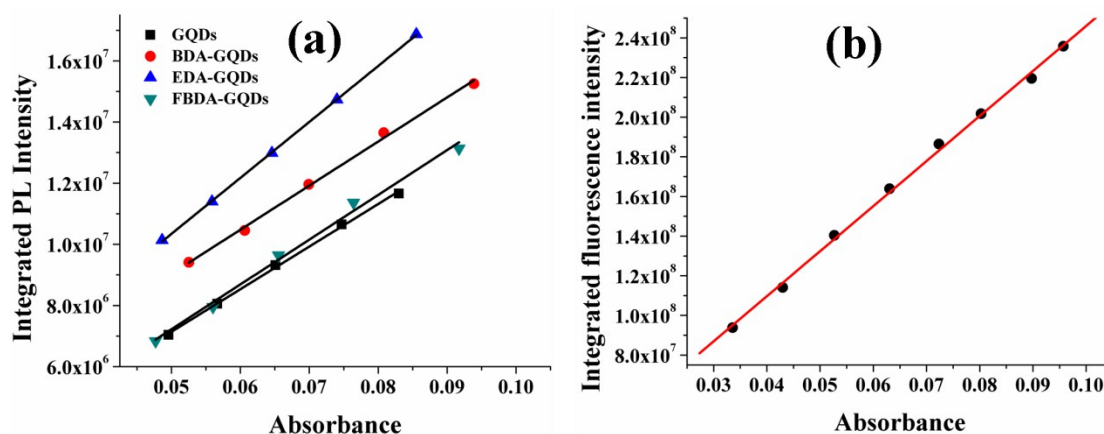


Figure S9. Plots of integrated fluorescence intensity (excited at 360 nm) against absorbance values at 360 nm of GQDs, EDA-GQDs, BDA-GQDs, FBDA-GQDs (a) and QS (b).

Table S2. The value of quantum yields of GQDs.

Samples	m	R	$\Phi_x = \Phi_{ST} (m_x/m_{ST}) (\eta_x/\eta_{ST})^2$
QS(reference)	2.27×10^9	0.999	$\Phi_{ST} = 54\%$ ($\eta_x = 1.33$, $\eta_{ST} = 1.33$)
GQDs	1.39×10^8	0.998	3.31%
EDA-GQDs	1.46×10^8	0.992	3.44%
BDA-GQDs	1.44×10^8	0.997	3.57%
FBDA-GQDs	1.83×10^8	0.999	4.35%

References

- [1] B. Delley, *J. Chem. Phys.*, 2000, **113**, 7756.
- [2] T. Yanai, D. P. Tew, N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51.
- [3] J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.*, 2005, **105**, 2999.