Supporting Information

Aryl-Modified Graphene Quantum Dots with Enhanced Photoluminescence and Improved pH Tolerance

Peihui Luo,[‖] Zhe Ji,[‖] Chun Li and Gaoquan Shi*

[‖]These authors contributed equally.
Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China.
E-mail: gshi@tsinghua.edu.cn

1. Fluorescence Quantum yield measurements

Fluorescence quantum yields (QYs) of GQDs were measured according the method reported in literature.[S1,S2] Optical density and photoluminescence (PL) intensity were measured by using a U-3010 UV-visible spectrometer (Hitachi, Japan) and a LS 55 fluorescence spectrometer (PerkinElmer), respectively. L-tyrosine aqueous solution (QY is 0.14) was selected as the reference. The following equation was used to calculate QY:

$$QY_s = QY_r(m_s/m_r)\,(n_s/n_r)^2$$

Where *QY* is quantum yield, *m* is the slope read from the linear plot of integrated PL intensity versus absorbance (**Figure S6**) and *n* is the refractive index of solvent. The subscript "s" and "r" refer to the sample and reference, respectively. The calculated results were shown in **Table S2.**

2. Estimation of grafting ratios

The grafting ratio was defined as the number of aryl groups grafted onto each TT-GQD. The estimation of grafting ratios was based on the atomic percentages of oxygen (O) of GQDs, because their sulfur (S) atom contents were too low (< 8%) and unreliable. The equation used for calculating grafting ratio is written as:

$$(N_{GQD} + rN_{aryl})At(O) = N(O)_{GQD} + rN(O)_{aryl}$$

were N_{GQD} and N_{aryl} were the number of total atoms in each TT-GQD and aryl graft, respectively; $N(O)_{GQD}$ and $N(O)_{aryl}$ are the numbers of O-atoms in each TT-GQD and aryl graft, respectively; r is the grafting ratio and $At(O)$ is the O-atom percentage of an aryl-modified GQD measured by XPS. To estimate N_{GQD} and $N(O)_{GQD}$, we supposed that the skeleton of each TT-GQD is a circular single-layer graphene sheet with a diameter of 2.5 nm, corresponding to an area of about 4.9 nm^2. Based on the graphene crystal structure, the average area for each carbon atom is calculated to be 0.026 nm^2; thus, a TT-GQD has about 187 carbon atoms. The atomic percentages of C and O in TT-GQD were measured to be 55.72 % and 30.58 %, respectively. Accordingly, N_{GQD} and $N(O)_{GQD}$ was calculated to be 336 and 103, respectively. In addition, $At(O)$ of SP-GQDs, SN-GQDs, CP-GQDs were measured by XPS to be 25.53 %, 23.46% and 23.10%, respectively. As a result, the grafting ratio of SP-GQDs, SN-GQDs and CP-GQDs is estimated to be about 21, 13 and 21, respectively.

3. Supplementary figures

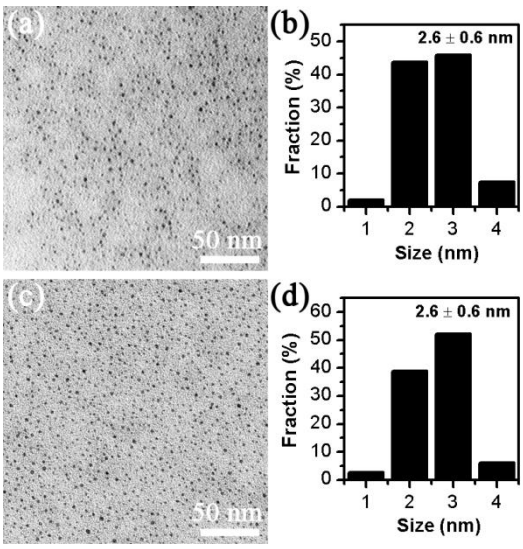

Figure S1. (a, c) TEM images of P-GQDs (a) and CP-GQDs (c); (b, d) the corresponding size distributions.

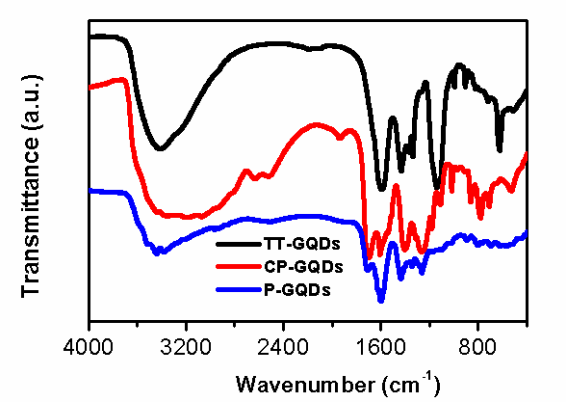

Figure S2. FTIR spectra of TT-GQDs, CP-GQDs and P-GQDs.

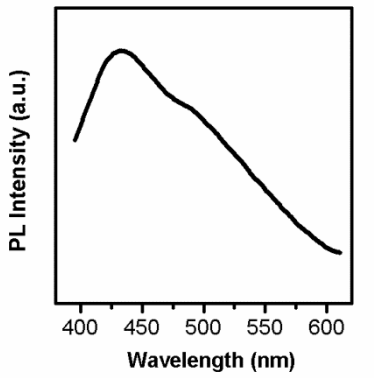

Figure S3. PL spectrum of an aqueous suspension of P-GQDs excited at 335 nm.

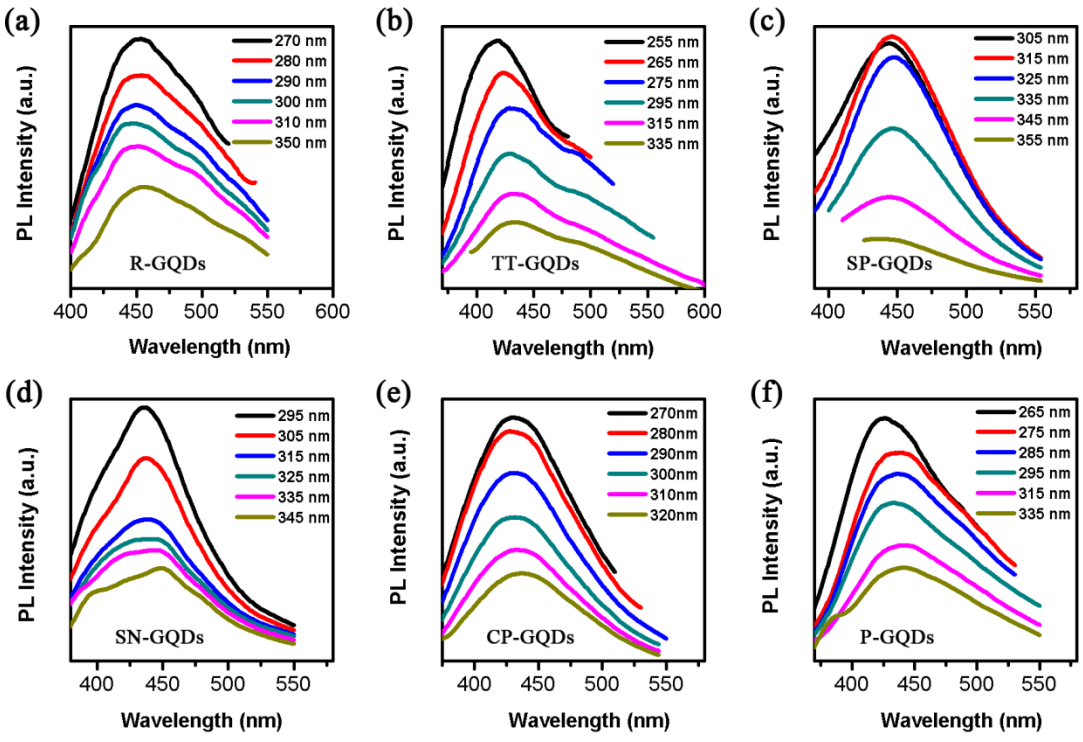

Figure S4. The PL spectra of the aqueous suspension of R-, TT-, SP-, SN-, CP- and P-GQDs recorded at different excitation wavelengths.

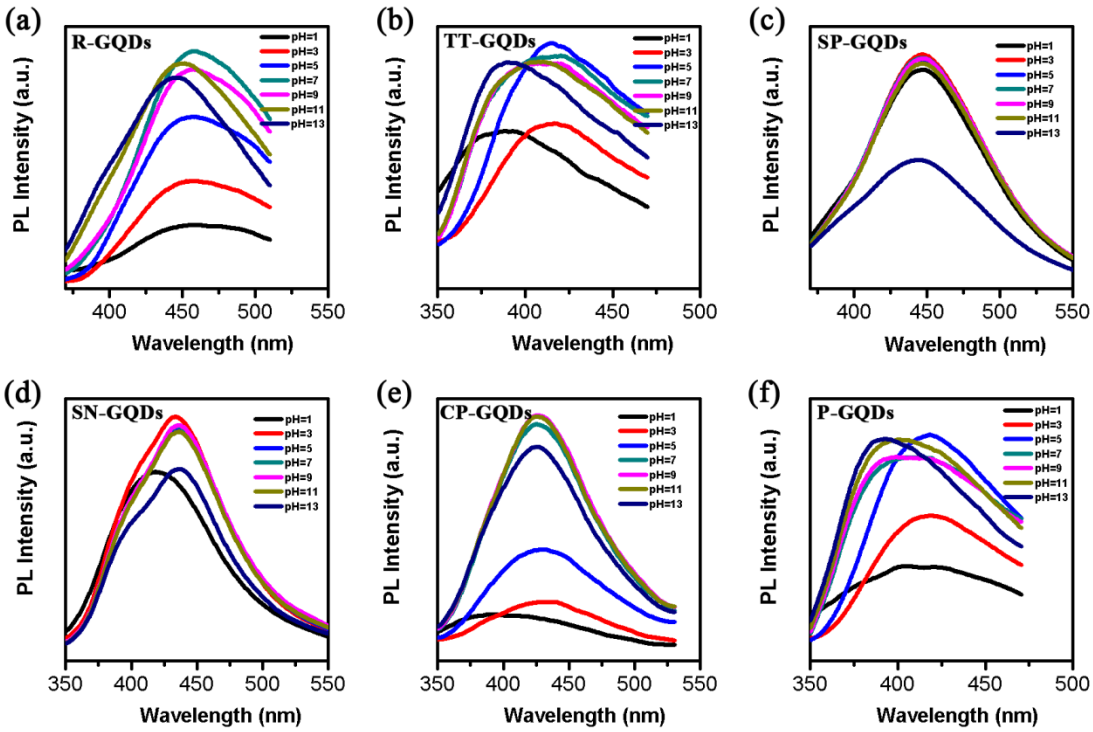

Figure S5. The pH-dependent PL behaviors of GQDs.

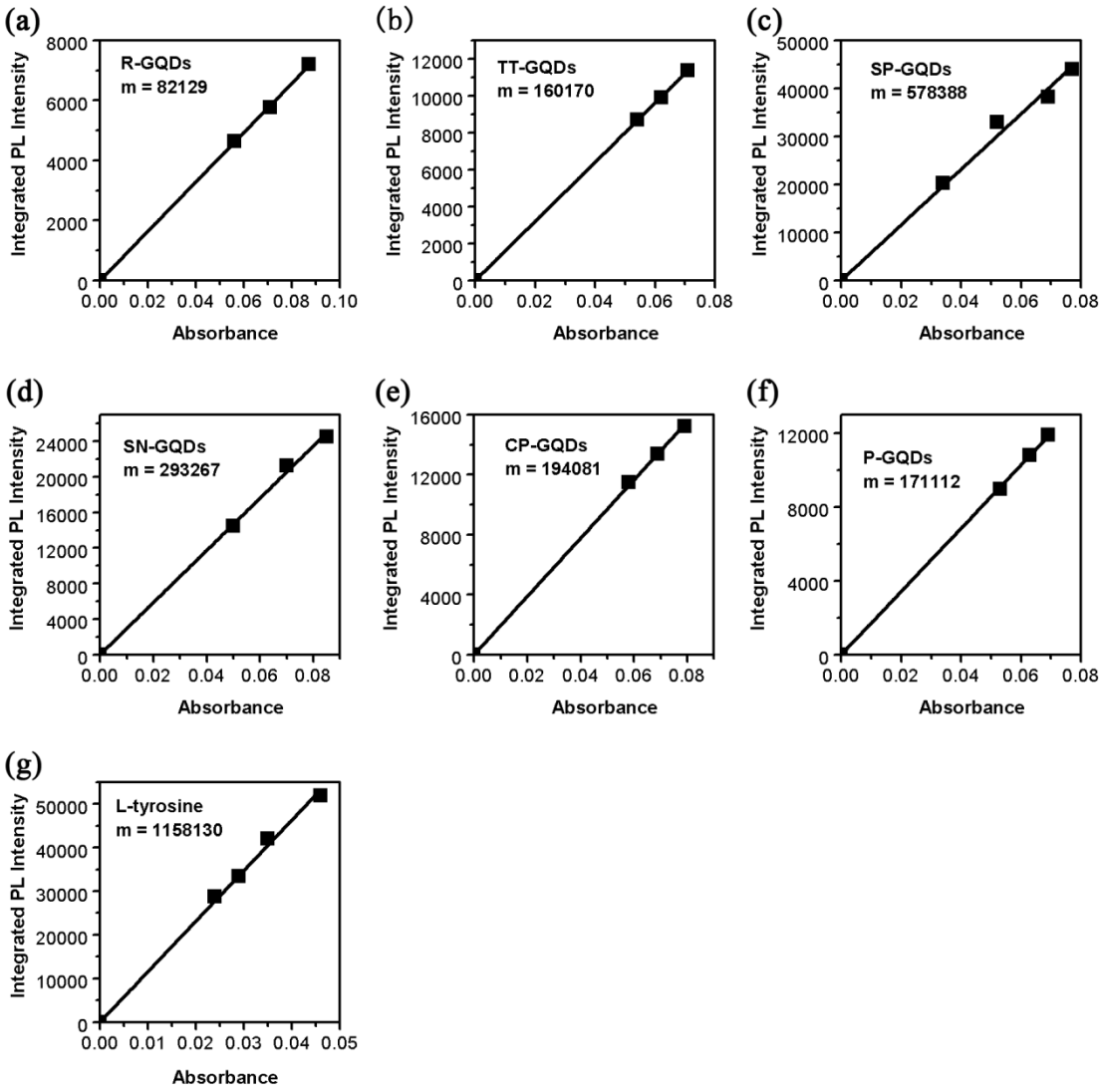

Figure S6. Plots of integrated PL intensity versus absorbance for different GQDs or L-tyrosine.

Table S1. Zeta potentials of GQDs

Sample	R-GQDs	TT-GQDs	SP-GQDs	SN-GQDs	CP-GQDs	P-GQDs
Zeta potential (mV)	–18.1	–21.4	–35.6	–19.1	–27.9	–22.5

Table S2. Fluorescence QY of GQDs using L-tyrosine as a reference[a]

Sample	Slope (*m*)	*QY* (%)
L-tyrosine	1158130	14.0
R-GQDs	82129	1.0
TT-GQDs	160170	1.9
SP-GQDs	578388	7.0
SN-GQDs	293267	3.5
CP-GQDs	194081	2.3
P-GQDs	171112	2.1

a: the refractive index of solvent (n) is 1.33

References:

S1 H. Zheng, Q. Wang, Y. Long, H. Zhang, X. Huang, R. Zhu, *Chem. Commun.*, 2011, **47**, 10650.

S2 D. Pan, J. Zhang, Z. Li, C. Wu, X. Yan, M. Wu, *Chem. Commun.*, 2010, **46**, 3681.