Electronic Supplementary Information

Revealing the tunable photoluminescence properties of graphene quantum qots

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Computational methods

All the calculations are carried out using Gaussian 09 suite of program.¹ The ground-state geometries of GQDs were firstly optimized by DFT²⁻³ B3LYP (Becke's three-parameter hybrid function⁴ with the non-local correlation of Lee-Yang-Parr⁵) method with the Pople 6-31G(d) basis set (B3LYP/6-31G(d)). The dangling carbon bonds are passivated by hydrogen atoms. The absorption spectra of GQDs were calculated using TDDFT method (at the B3LYP/6-31G(d) level) based on optimized ground-state geometries. The first excited state was optimized using TDDFT method to calculate the emission energy (wavelength) which is the energy difference between the ground and the first excited state.

References

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Fig. S1. Structure of hexagonal GQDs with zigzag edge (G1-G6) and armchair edge (G7-G8).

GQDs		$E_{\rm gap} ({\rm eV})^a$	Eemission	Wavelength	Color
			(eV)	(nm)	
G1: Benzene	0.46 nm	6.81	5.27	235.2	DUV
G2: Coronene	0.92 nm	4.04	3.10	399.5	Violet
G3:Ovalene	1.05 nm	2.93	2.52	492.0	Green
G4: Cir-coronene	1.39 nm	2.82	2.17	572.4	Green
G5	1.85 nm	2.12	1.62	765.2	Red
G6	2.31 nm	1.64	1.24	999.5	Near IR
G7: HBC	1.27 nm	3.59	2.75	450.5	Blue
G8	2.06 nm	2.37	1.83	678.2	Red

Table S1. Calculated Ground-state Band Gap (E_{gap}) , Emission Energy, and EmissionWavelength of GQDs

 ${}^{a}E_{gap}$ is the ground-state HOMO-LUMO energy gap.



Fig. S2. Molecular orbitals for HOMO and LUMO of zigzag and armchair-edged GQDs. Molecular orbitals are concentrated on edge sites in zigzag-edged GQDs but scattered in the center in armchair-edge GQDs. G-S1 is 2.87 nm armchair-edged GQD. Values in the parentheses are orbital energies in eV.



Fig. S3. Heterogeneously hybridized GQDs with differently sized sp² domains. (a) composed of four coronene (G2) and (b) four cir-coronene (G4) domains. The GQD ($C_{154}H_{90}$) and ($C_{320}H_{150}$) have ground-state band gap of 3.73 and 2.68 eV, respectively.



Fig. S4. Heterogeneously hybridized GQDs with identifically sized sp² domains. (a) 3.26 nm $C_{294}H_{168}$ GQD and (b) 5.54 nm $C_{864}H_{480}$ GQD composed of seven and nineteen coronene (G2) domains, respectively.