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Supporting Information for

$C_{96}H_{30}$ Tailored Single-layer and Single-crystalline Graphene Quantum Dots

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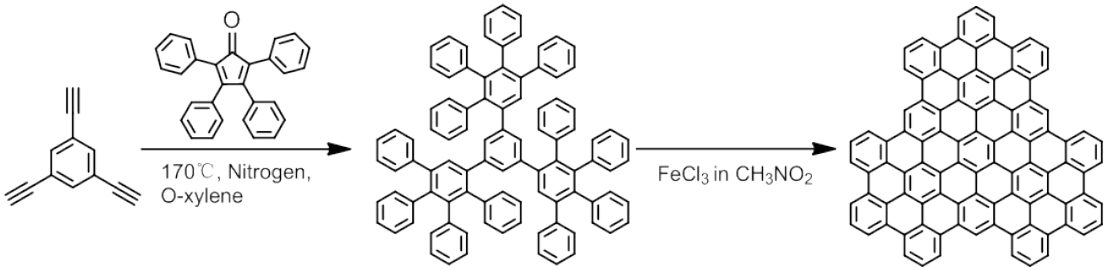

Fig. S1 Synthesis progress of $C_{96}H_{30}$

Synthesis progress of $C_{96}H_{30}$: 1,3,5-Triethynylbenzene (0.15 g) and tetraphenylcyclopentadienone (1.4 g) were dissolved in o-xylene (20 mL) under a nitrogen atmosphere. The mixture was heated at 170 °C under magnetic stirring and reflux condensation for 10 h. After cooling, n-heptane (100 mL) was added into the mixture. The products were collected by vacuum filtration and washed by n-heptane and ethanol. The obtained $C_{96}H_{66}$ was ca. 0.62 g after vacuum drying at 100 °C for 24h. Then, $C_{96}H_{66}$ (0.4 g) was dissolved in dry dichloromethane (200 mL) and nitrogen continuously bubbled through the solution. Then dry iron (III) chloride (3 g) dissolved in nitromethane (10 mL) was dropwise added by a funnel. The reaction was kept for 24 h and replenished

the dichloromethane to keep the volume dose. Then, the reaction was quenched by adding methanol (300 mL). The precipitate was collected by filtration and washed successively with methanol and dichloromethane each for three times. A yellow-brown solid was obtained after vacuum drying at 100 °C for 24 h.

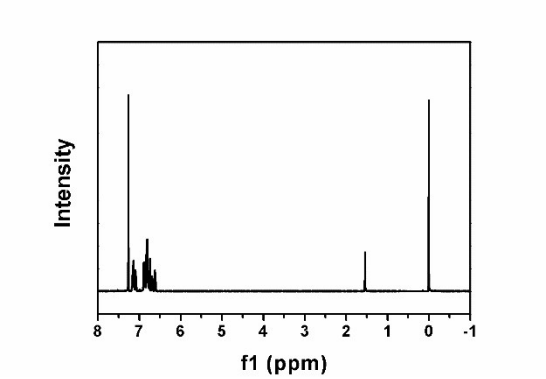

Fig. S2 ^{1}HNMR spectra of $C_{96}H_{66}$, solvent: $CDCl_3$

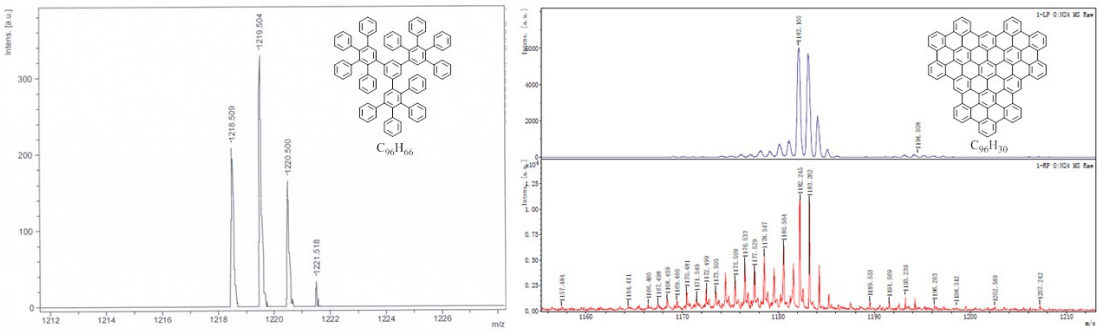

Fig. S3 Mass spectra of (a) $C_{96}H_{66}$ and (b) $C_{96}H_{30}$

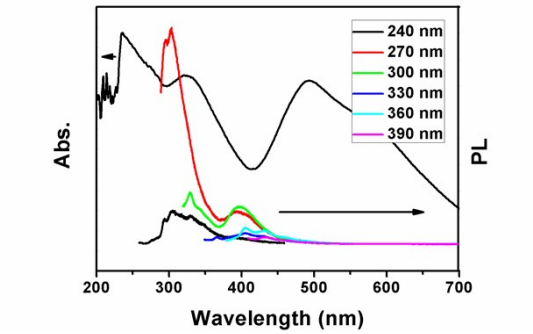

Fig. S4 Absorption and PL spectra under different excitation wavelength of $C_{96}H_{30}$.

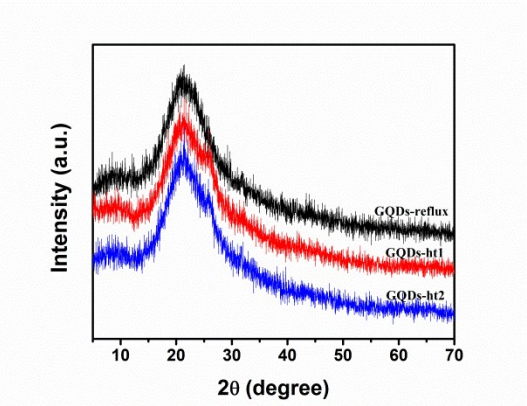

Fig. S5 XRD of GQDs-reflux, GQDs-ht1 and GQDs-ht2

The obtained GQDs are showing a broad peak at 21.6° corresponding to the graphene (002) planes. The (002) lattice spacing were 0.41 nm which were higher than the graphite (0.334 nm) because of their higher oxygen contents.

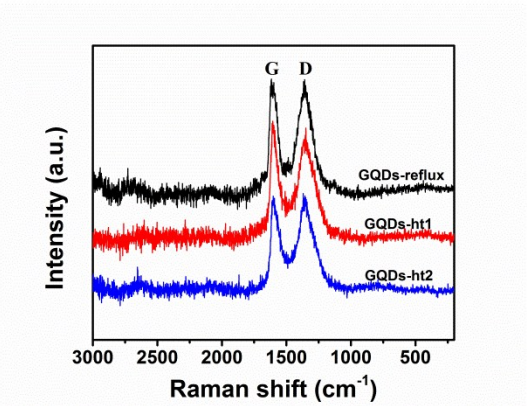

Fig. S6 Raman spectrum of GQDs-reflux, GQDs-ht1 and GQDs-ht2

The G peak at 1600 cm^{-1} corresponds to the E 2g mode of graphite and is related to the vibration of the sp2-bonded C atoms in a two-dimensional hexagonal lattice, while the D peak at 1360 cm^{-1} exhibits disorder due to scattering at the edges. The relative intensity of D/G band are almost 1.

Table S1 The amounts of functional groups of each GQDs by XPS

Sample	C-C	C-N	C-OH	C-O-C	COOH	C=O	COO^-
GQDs-reflux	56.9%	8.7%	1.8%	22.2%	10.3%		
GQDs-ht1	70.3%		1.1%	12.7%		7.4%	8.5%
GQDs-ht2	61.8%		8.1%	9.9%		17.4%	2.7%

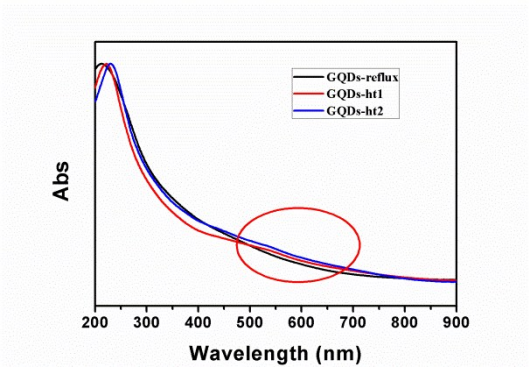

Fig. S7 Normalized UV-vis absorption spectrum of GQDs-reflux, GQDs-ht1 and GQDs-ht2

A new absorption band at 500-700 nm of GQDs-ht1 and GQDs-ht2 were observed, which are responsible for the quinone structure.

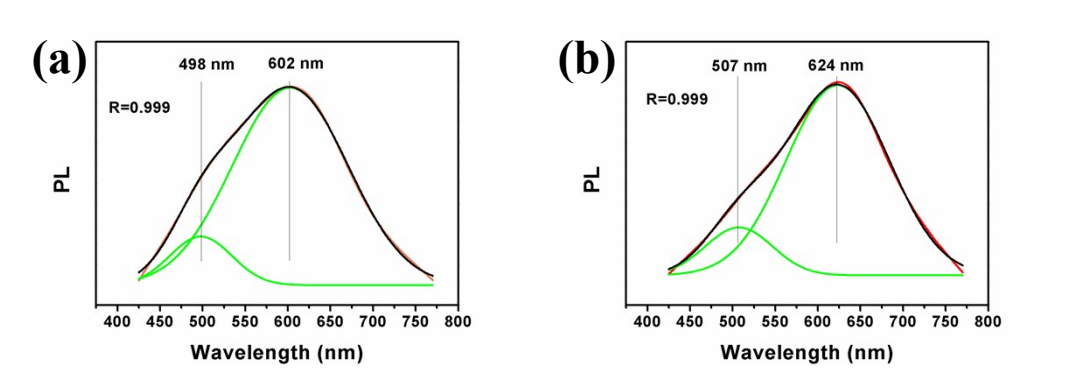

Fig. S8 Gaussian fitting curves of PL spectra excited at 400 nm (a: GQDs-ht1 and b: GQDs-ht2)

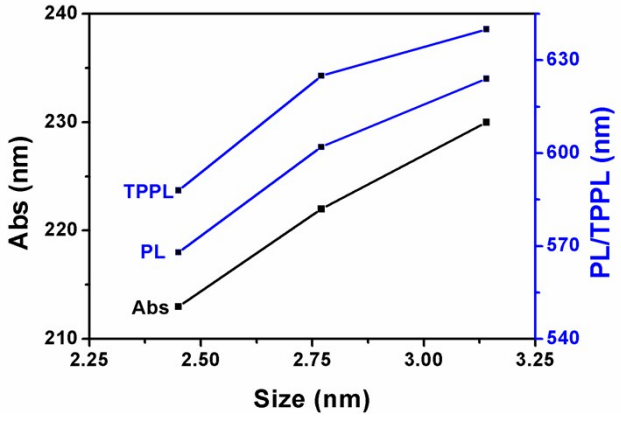

Fig. S9 The size-dependent effect of absorption, PL and TPPL

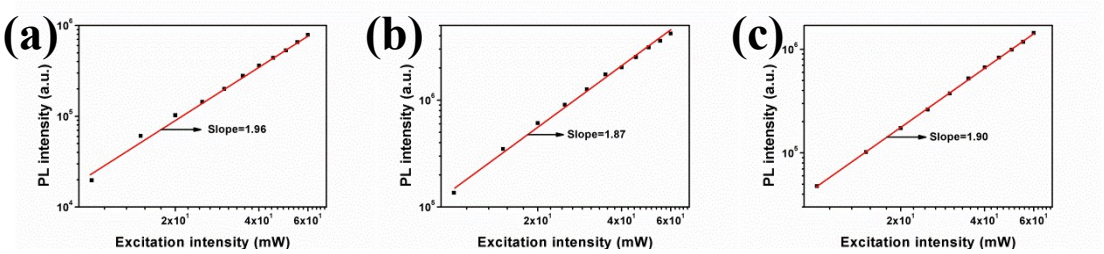

Fig. S10 Relationship of the TPPL intensities with excitation laser power at 800 nm, (a) GQDs-reflux, (b) GQDs-ht1 and (c) GQDs-ht2.

The slopes in the logarithmic curves are approximate 2 for all the three samples, which confirm the TPA properties.

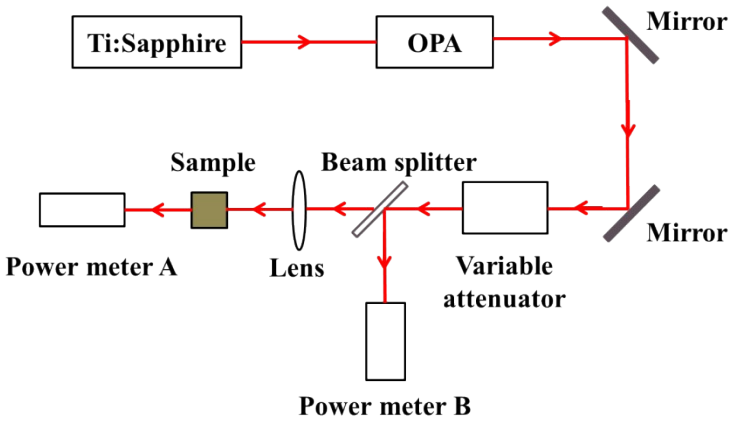

Fig. S11 Experimental setup used in NLT measurement

The pump laser beam came from a Ti:sapphire system with optical parameter amplifier (OPA). The output wavelength, pulse duration and repletion rate were 800 nm, ~130 fs and 1 kHz, respectively. GQDs samples were dissolved in deionized water with a linear transmittance of 70% at 800 nm.