Electronic Supplementary Information

for

A surfactant-assisted redox hydrothermal route to prepare highly photoluminescent carbon quantum dots with aggregation-induced emission enhancement properties

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concentrations of CTAB and the as-prepared CQDs.

13. **Figure S11.** PL spectra of as-prepared CQDs (a), carboxyl CQDs (b), N-doped CQDs (c) and Rh 6G (d) dissolved in different fractions of glycerol/water mixture. Figure S10e was the viscosities of different glycerol fractions in glycerol/water mixtures.

14. **Figure S12.** NaCl influence on the PL intensity (a) and DLS intensity (b) of CQDs.

15. **Figure S13.** Solvents influence on the PL intensity of CQDs.

Experimental Section

Reagents and Chemicals. All reagents and solvents were obtained from commercial sources and used as received unless otherwise statement. [60] Fullerene (C_{60}) was purchased from Aladdin Chemistry Co., Ltd (Shanghai, China). Sodium Hydroxide and hydrogen peroxide were purchased from Chuandong Chemical Group Co., Ltd (Chongqing, China). Cetyltrimethyl Ammonium Bromide (CTAB) and glycerol were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Adenosine-5'-triphosphate (ATP) was purchased from Sigma-Aldrich Co. LLC. (USA). Ultrapure water (18.2 MΩ) which prepared with a Milli-Q system (Millipore, Bedford, MA, USA) was used throughout the experiments. All reagents were used as received unless otherwise statement.

Characterization. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were recorded with Tecnai G2 F20 S-TWIN microscopy (FEI, USA) and S-4800 Scanning electron microscopy (Hitachi, Japan). Atomic force microscopy (AFM) images were obtained from a Vecco multimode Nanoscope TM scanning probe microsystem (Vecco, USA) with TESP7 tips. Waters 515 gel permeation chromatograph (Waters, USA), Waters 2414 refractive index detector (Waters, USA) and ultrahydrogel linear 7.8×300 mm column (Waters, USA) were used to recorded the gel permeation chromatogram (GPC) spectrum, current speed was maintained at 0.5 mL min^{-1} and column temperature was maintained at 35 ^{o}C. A FTIR-8400S Fourier transform infrared (FT-IR) spectrophotometer (Shimadzu, Japan) was used to record the IR spectra. An

ESCALAB 250 X-ray photoelectron spectrometer (Thermo, USA) was used for recording XPS spectra. Absorption and PL spectra were measured at room temperature with a 3600 UV-Vis-NIR spectrophotometer (Shimadzu, Japan) and a 2500 fluorescence spectrophotometer (Hitachi, Japan), respectively. ^{1}H and ^{13}C NMR spectra were recorded with AV-300 spectrometer (Bruker, German). Dynamic Light Scattering (DLS) data were recorded with Nano-ZS spectrometer (Malvern, UK). Raman spectrum was taken using a LabRAM HR 800 Raman spectrometer (Horiba Jobin Yvon Inc., France). PL lifetimes were measured using a fluorolog-3 fluorescence spectrometer (Horiba Jobin Yvon Inc., France). An Olympus E-510 digital camera was used to capture the photographs of solutions. Ubbelohde viscometer was used to measure the viscosity of different glycerol/water mixtures.

Preparation of CQDs. The CQDs were synthesized by a hydrothermal method from C_{60}. In a typical procedure, 20 mL *p*-polyphenylene doped Teflon-lined stainless steel autoclave was cleaned in a bath of fresh aqua regia and rinsed thoroughly in H_2O before using. Then 10 mg C_{60}, 0.1 g NaOH, 0.1 g CTAB, 0.1 mL 1% H_2O_2 and 5.9 mL H_2O were added in. The autoclave was maintained at 150 ^{o}C for 1 hour. After the autoclave cooled down naturally, the brown solution was centrifuged at 12000 rpm for 10 minutes. Then the supernatant which contained with CQDs was transferred into the EP tube.

As for other five CQDs derivatives, the substrates were as follow: (1) 10 mg C_{60} and 6.0 mL H_2O; (2) 10 mg C_{60}, 0.1 g NaOH and 6.0 mL H_2O; (3) 10 mg C_{60}, 0.1 g NaOH, 0.1 mL 1% H_2O_2 and 5.9 mL H_2O; (4) 10 mg C_{60}, 0.1 g CTAB and 6.0 mL H_2O; (5)

10 mg C_{60}, 0.1 g NaOH, 0.1 g CTAB and 5.9 mL H_2O. The reaction conditions were the same as mentioned above.

CTAB Sensitized Effect. two kinds of CQDs were prepared in this part. The first one was the highly photoluminescent CQDs which prepared follow the mentioned procedure. The synthesis procedure for the second CQDs referred to the (3) CQDs derivative. The second CQDs were mixed with different concentrations of CTAB. The final concentrations of CTAB from 1 to 8 are 0, 2.8, 5.6, 8.4, 11.2, 14.0 16.8 mg mL^{-1}, respectively. Then the PL intensities of the first CQDs and the second CQDs which mixed with different concentrations of CTAB were measured by fluorescence spectrophotometer.

Sample Preparation. For viscosity effect test, 990 μL different fractions glycerol/water mixture, 10 μL CQDs solution (about 1 mg mL^{-1}) or 10 μL Rhodamine 6G (Rh 6G, 5×10^{-4} M) were added in a 1.5 mL EP tube. Then the solution was vortexed thoroughly to make sure it was blended. The solution was settled for 30 minutes to wipe off bubbles, and then transferred for PL measurement.

For nanoparticles aggregation induced emission enhancement (NPs-AIEE), 10 μL CQDs solution (about 1 mg mL^{-1}) and 990 μL different concentration of ATP solution or different solvents were added in a 1.5 mL EP tube. Then the solution was vortexed thoroughly and transferred for PL measurement.

Quantum Yield Calculation. The quantum yield (Φ) of CQDs was obtained by comparing the integrated PL intensities and the absorbance values of the CQDs with the reference quinine sulfate. The CQDs was dissolved in water (refractive index $\eta =$

1.33) and quinine sulfate (literature $\Phi_R = 0.54$) was dissolved in 0.1 mol/L H_2SO_4 (refractive index $\eta = 1.33$). These methods were reported to be used to measure the quantum yield of carbon nanoparticles.[1-3]

Method 1: A certain concentration of CQDs and the quinine sulfate were made, all of which had absorbance less than 0.1 at the excitation wavelength of CQDs.
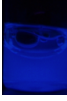
$$\Phi = \Phi_R \times \frac{A_R}{A} \times \frac{I}{I_R} \times \frac{\eta^2}{\eta_R^2} \qquad (1)$$

Method 2: Different concentrations of CQDs and the quinine sulfate were made, all of which had absorbance less than 0.1 at the excitation wavelength of CQDs.

$$\Phi = \Phi_R \times \frac{m}{m_R} \times \frac{\eta^2}{\eta_R^2} \qquad (2)$$

Where A is the absorbance and I refers to the integrated PL intensity, m is the slopes determined by the curves in Figure S1, η is the refractive index of the solvent, for these aqueous solutions, $\eta^2 / \eta_R^2 = 1$. The subscript of R refers to the reference.

Table 1. Properties of different CQDs derivatives.

Substrate	Ex / Em (nm)	$< \tau >$ (ns) [c]	Φ	k_r (10^6 s^{-1}) [d]	k_{nr} (10^8 s^{-1}) [d]	Photo Image Daylight	UV
C$_{60}$ [a]	300 / 384	4.00	0.0293	7.32	2.43		
C$_{60}$ + NaOH [a]	300 / 394	2.35	0.0174	7.40	4.18		
C$_{60}$ + NaOH + H$_2$O$_2$ [a]	300 / 394	2.37	0.0116	4.89	4.17		
C$_{60}$ + CTAB [a]	340 / 399	1.18	0.3020	256	5.92		
C$_{60}$ + NaOH + CTAB [b]	320 / 396	1.36	0.3892	286	4.49		
C$_{60}$ + NaOH + H$_2$O$_2$ + CTAB [b]	320 / 395	1.23	0.5223	425	3.88		

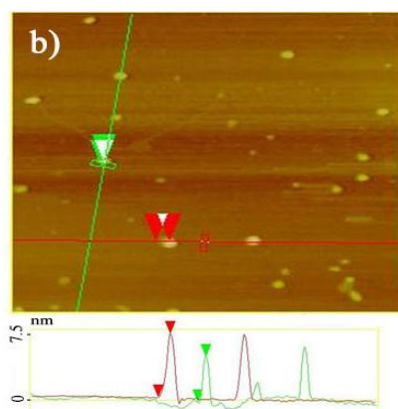[a] The PLQY was measured and calculated by method 1. [b] The PLQY was measured and calculated

by method 2. [c] PL average lifetime was calculated according to the formula of $< \tau > = (\sum \alpha_i \tau_i) / \sum \alpha_i$.

[d] Rate constants were calculated with Φ and τ according to the formula of $k_r = \Phi / \tau$ and $k_{nr} = (1 - \Phi) / \tau$.
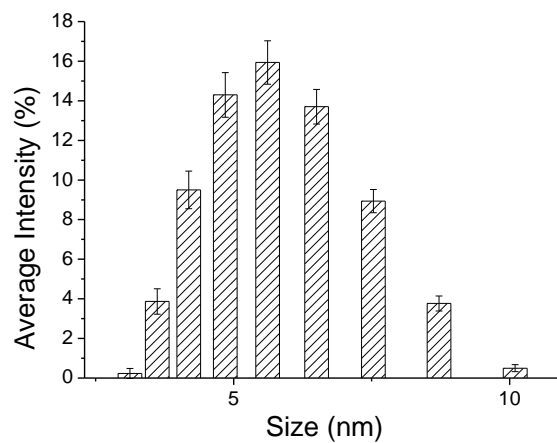
τ.
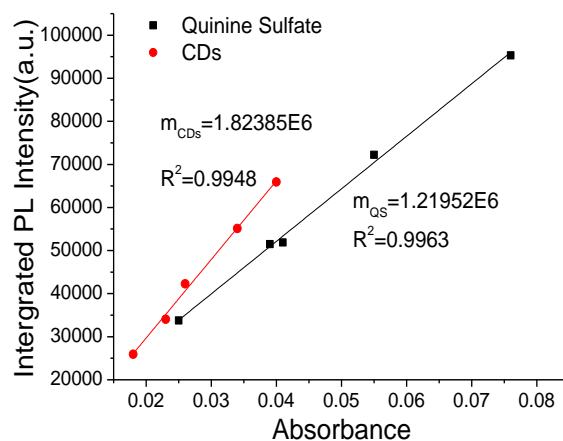
Figure S1. Linear fitting for quantum yield calculation of CQDs and Quinine sulfate.

Figure S2. A representative AFM image of the CQDs and the height analysis along the green and red

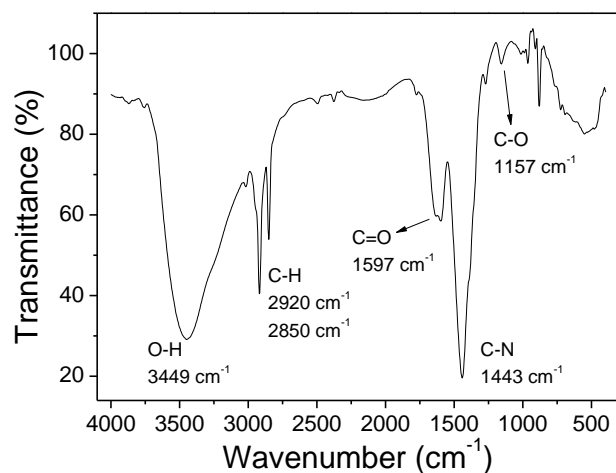lines in the AFM image. The result indicated that the height of CQDs was approximate 5 nm.

Figure S3. The DLS of the CQDs. The result indicated the average particle size was approximately 6

nm, which corresponded to the TEM and AFM data.
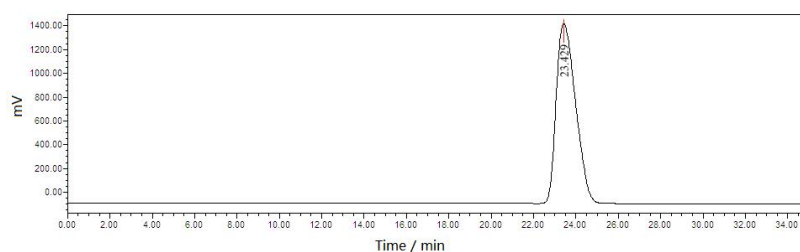
Figure S4. The GPC spectrum of the CQDs. The result indicated the uniformity of as-prepared CQDs.

Figure S5. FTIR spectrum of the CQDs. A strong wide peak at 3449 cm^{-1} indicating the presence of O-H, while the peaks at 1597 and 1157 cm^{-1} exhibited characteristic absorption bands of C=O and C-O stretching vibrations, respectively, which proved the existence of hydroxyl and carbonyl groups on the surface of CQDs. Peaks at 2920 cm^{-1}, 2850 cm^{-1} and 1443 cm^{-1} in FT-IR were attributed to the stretching vibration of C-H and C-N, which were partly aroused by CTAB.
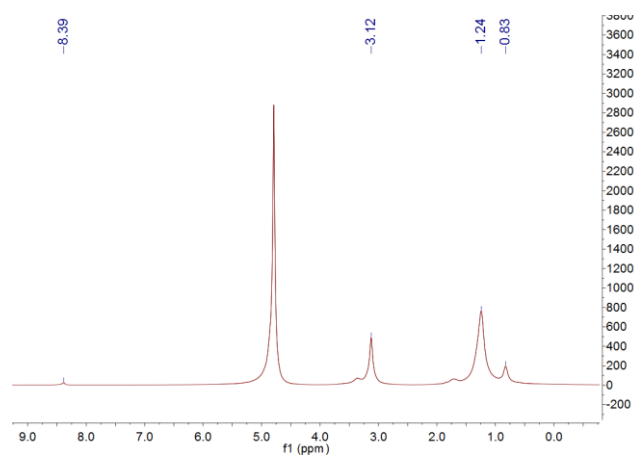
**Figure S6.** ^{1}H NMR spectrum of CQDs. The chemical shift of 3.12 in ^{1}H NMR should be aroused by -OH. ^{1}H-NMR (300MHz, D$_2$O): δ 8.39 (br, -COOH); 3.12 (s, -OH); 1.24 (s, -CH); 0.83 (s, -CH$_3$).
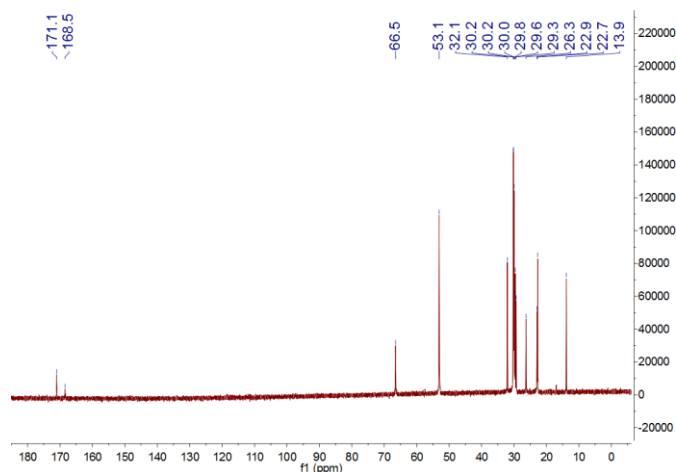
**Figure S7.** ^{13}C NMR spectrum of CQDs. An apparent signal at a chemical shift of 171.10 ppm assigned to –COOH.
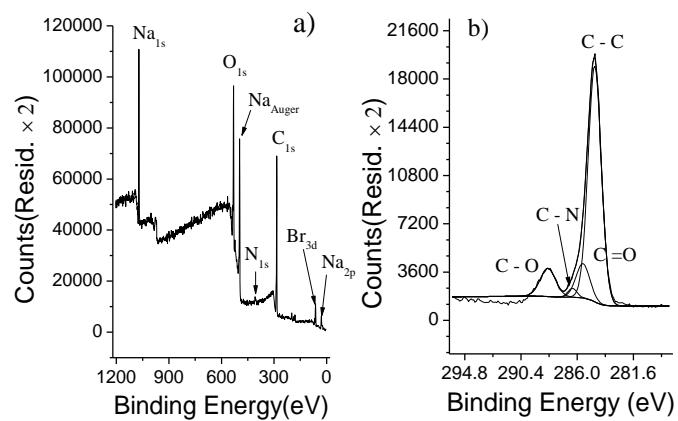
Figure S8. a) XPS spectrum of CQDs. Peaks at 1071, 532, 400 and 285 eV were attributed to the Na_{1s}, O_{1s}, N_{1s} and C_{1s}, respectively. b) The fitting C_{1s} spectrum. Four peaks at 284.6, 285.6, 286.4 and 288.3 eV were attributed to C-C, C-N, C-O and C=O, respectively.
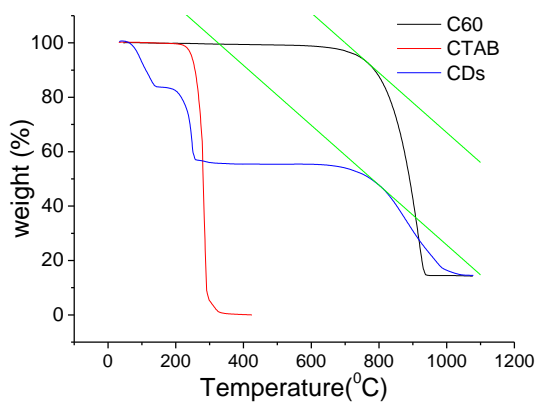
Figure S9. TGA data of the pure C_{60}, CTAB and the as-prepared CQDs. The two green lines are indicated the weight-losing points of the curves, which have the same slope. The weight-losing point of CQDs was approximately 30 ^{o}C higher than the pure C_{60}. Also, the slope of CQDs in the range of 800 ^{o}C to 1100 ^{o}C was smaller than that of pure C_{60}. The result indicated that the CQDs were more thermal stable than pure C_{60}. That is committed to the idea that the CQDs were not simple combinations of C_{60} and CTAB, and reactions were happened so that CTAB was attached to the CQDs.
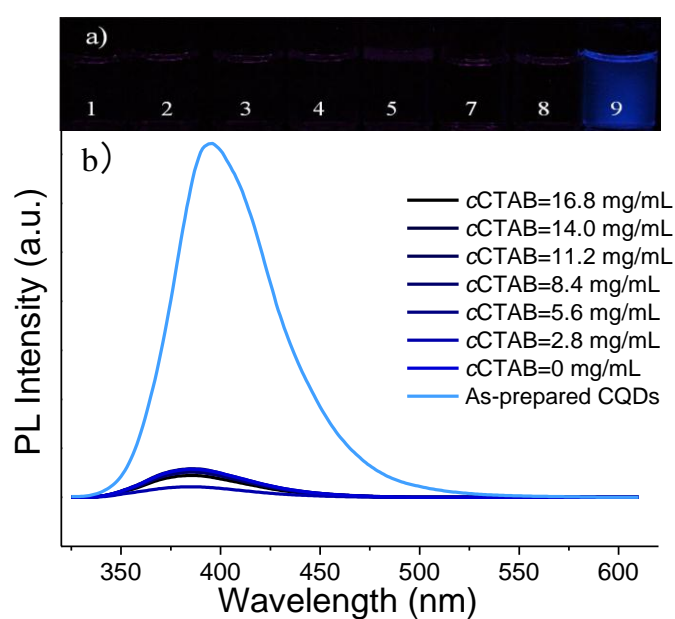
Figure S10. PL responses of non-CTAB CQDs which mixed with varies concentrations of CTAB and the as-prepared CQDs. a) optical images of non-CTAB CQDs mixed with different concentrations of CTAB (from No. 1 to No. 8) and the as-prepared CQDs (No. 9). The concentrations of CTAB from 1 to 8 are 0, 2.8, 5.6, 8.4, 11.2, 14.0 16.8 mg mL^{-1}, respectively, and the PL intensity remained constant, which could be clearly figured out from the PL spectra b) PL spectra of non-CTAB CQDs mixed with different concentrations of CTAB and the as-prepared CQDs.
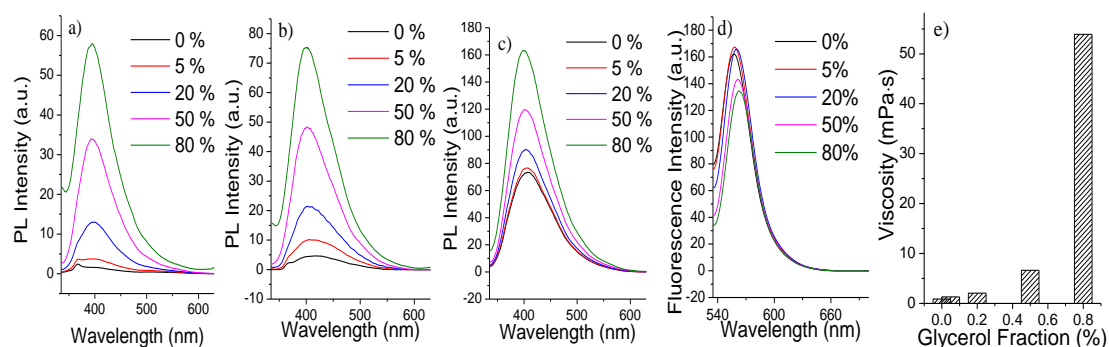
Figure S11. a) PL spectra of as-prepared CQDs dissolved in different fractions of glycerol/water mixture; b) PL spectra of other carboxyl CQDs dissolved in different fractions of glycerol/water mixture; c) PL spectra of N-doped CQDs dissolved in different fractions of glycerol/water mixture. d) Fluorescence spectra of Rh 6G dissolved in different fractions of glycerol/water mixture. e) Viscosities of different glycerol fractions in glycerol/water mixtures. Glycerol fractions in turn were 0%, 5%, 20%, 50%, 80%. Concentration: [Rh 6G] = 4×10^{-6} M.
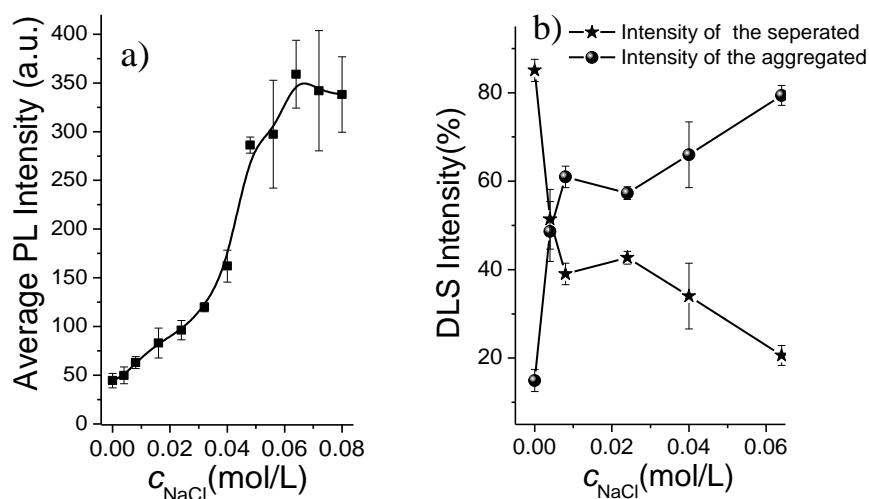
Figure S12. NaCl influence on the PL intensity (a) and DLS intensity (b) of CQDs. NaCl neutralized the charge of CQDs, which could result the aggregation. The PL intensity and DLS were measured to confirm the aggregation. The PL spectra showed that by increasing the salt concentration, PL intensities could be efficiently enhanced for approximately 7 times, and reached a plateau when salt concentration was 0.064 M (Figure S12a). Meantime, the DLS data of those solutions was measured,

and the result indicated there were two major diameters: One was about 5 nm which was the diameter of the separated CQDs. The other one was larger than 100 nm which should be the aggregated. With the increasing of the concentration of NaCl, the proportion of the aggregated became larger, but the separated became less (Figure S12b). This result also proved the AIEE phenomenon from CQDs. Concentration: [CQDs] = 40 μg / mL, [NaCl] = 0, 0.004, 0.008, 0.024, 0.04 and 0.064 M
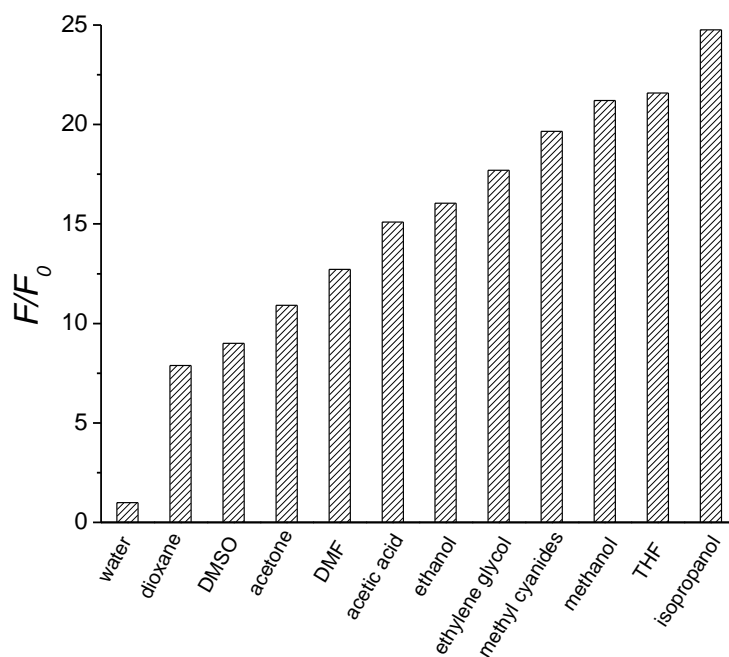
Figure S13. Solvents influence on the PL intensity of CQDs. All the tested organic solvents, no any exception, could significantly enhance the PL emission of the CQDs. The PL intensity of CQDs in water was settled as F_0 in the comparison. Concentration: [CQDs] = 70 μg / mL,

1. D. Pan, J. Zhang, Z. Li, C. Wu, X. Yan and M. Wu, *Chem. Commun.*, 2010, **46**, 3681-3683.
2. J. Zhou, C. Booker, R. Li, X. Zhou, T.-K. Sham, X. Sun and Z. Ding, *J. Am. Chem. Soc.*, 2007, **129**, 744 - 745.
3. L. Lin and S. Zhang, *Chem. Commun.*, 2012, **48**, 10177-10179.