Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

A Srikaya-like Light Harvesting Antenna Based on Graphene Quantum Dots and Porphyrin Single Molecular Micelles

Yannan Liu, Shanlong Li, Yongli Zheng, Meng Zhang, Caiyun Cai, Chunyang Yu, Yongfeng Zhou* and Deyue Yan*

School of Chemistry and Chemical Engineering, State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, 800 Dong chuan Road, Shanghai 200240 (China)
E-mail: yfzhou@sjtu.edu.cn, dyyan@sjtu.edu.cn

1. Materials

Dimethylformamide (DMF), dichloromethane (CH_2Cl_2) were purified with CaH_2. Terahydrofuran (THF) was firstly purified with CaH_2 and it was further distilled with sodium wire before use. Pyrrole (Adamas) and 2-(Dimethylamino)ethyl methacrylate (DMAEMA, Adamas) were distilled under reduced pressure to remove polymerization inhibitor. KH in mineral oil are obtained from Acros Company and washed by distilled THF for 5 times. All the other chemicals were purchased from Sinopharm Chemical Regent Company (SCRC) and used as received.

2. Instruments and Measurements

Nuclear Magnetic Resonance (NMR)

^1H NMR spectra were recorded using Bruker AVANCEIII 400 spectrometer with dimethylsulfoxide-d_6 as solvents at 293K. Tetramethylsilane (TMS) was used as an internal standard.

Dynamic Light Scattering (DLS) and Zeta Potentials

DLS and Zeta potentials of samples were measured using a Malvern Zetasizer Nano ZS90 (Malvern Instruments, Ltd.) equipped with a 4 mW He-Ne laser light. The scattering angle of DLS measurement is 90º.

Transmission Electron Microscopy

TEM measurements were performed with a FEI Tecnai G2 Spirit Biotwin instrument at a voltage of 120 kV. The TEM samples were prepared by depositing one drop of solutions onto carbon-coated copper screen, and it was dried in air for 24h.

High Resolution Transmission Electron Microscopy (HRTEM)

HRTEM measurements were performed with a JEOL JEM-2100F instrument at a voltage of 200 kV. The samples were prepared using the same method with the TEM measurements.

Ultraviolet-visible (UV-vis) Absorption Spectra

The UV-vis absorption spectra of sample were measured at 298K in the range of 300-800 nm on a Perkin Elmer Lambda 20 UV-vis spectrometer. The sample solutions were added to a 1cm quartz cuvette for the measurements.

Fluorescence Spectra and Time-resolved Fluorescence Spectra

The fluorescence spectra and time-resolved fluorescence spectra measurements were recorded on a PTIQM/TM/IM steady-state & time-resolved fluorescence spectro-fluorometer (USA/CAN Photon Technology International Int.). The solution of samples were added to a 1cm quartz cuvette for the measurements.

X-ray photoelectron spectra (XPS)

The X-ray photoelectron spectra were conducted on X-ray photoelectron spectroscopy (Thermo Fisher Scientific, UK) to determine the element contents. Since GQDs aqueous solution are dripped on aluminum foil and dried for XPS, so there are some impurities in binding peaks.

Fourier Transform Infrared Spectrum (FTIR)

FTIR spectra were recorded on a Perkin Elmer Paragon 1000 spectrophotometer between 450 and 4000 cm^{-1}. Samples were prepared by grinding the solid sample with potassium bromide (KBr) under high pressure.

4. Preparation of GQDs

GQDs were prepared byreported methods.[1,2] Firstly, 250 mg graphene oxide (GO) was dispersed in10 mL DMF, which were dispersed under ultrasonic condition for 30 minutes (200 kHz), and the mixed solution was transferred to a poly (tetrafluoroethylene) (Teflon) reactor (20 mL) and heated at 200 ºC for 8 h. And then the reactors were cooled toroom temperature naturally. Gradientcolumn was used to purify the transparent suspension (mobile phase A and B are methylene chloride/ MeOH (2:1, V/V) and H_2O, respectively). As a result the GQDs solution with a yield of ca. 30% was obtianed. And the GQDs solution can be diluted by adding deionized water or concentrated by reduced pressure distillation.

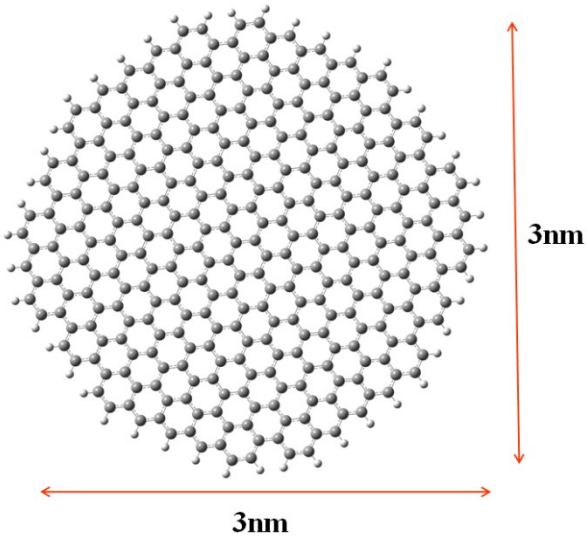

Fig. S1 The 3D molecular simulation of one layer of GQDs. (324 C atom and 46 H atom)

According to the literature,[1,2] the average height of GQDs is about 1.0 nm. Since the distance between the layers of graphene is 0.34 nm. That is to say, there is about 4 layers graphene in every GQDs. Combining with the size of GQDs about 3 nm, the molecular weight of every GQDs can be calculated roughly to be 15 kD. And the concentration of GQDs solution was obtained by drying a certain volume of GQDs aqueous solution and the obtained solid powder was weighed. Then we can approximately estimate the amount of GQDs per milliliter. It should be noted that the functional group in GQDs was not counted, so it can inevitably cause some error using this method.

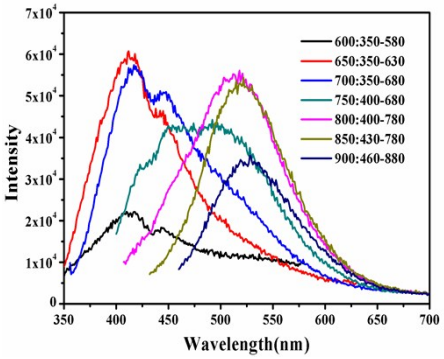

Fig. S2 The up-conversion fluorescence spectra of GQDs.

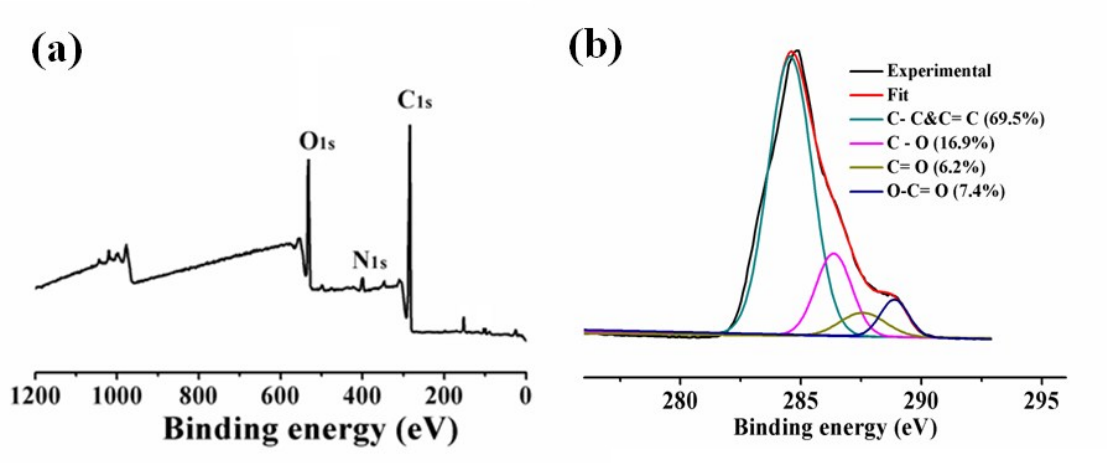

Fig. S3 a**) XPS** spectrum of GQDs, b) Peak-differentiating and imitating of C_{1s} peak of GQDs.

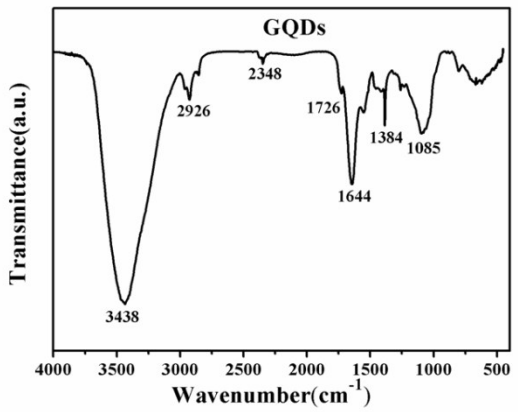

Fig. S4 The FTIR spectrum of GQDs.

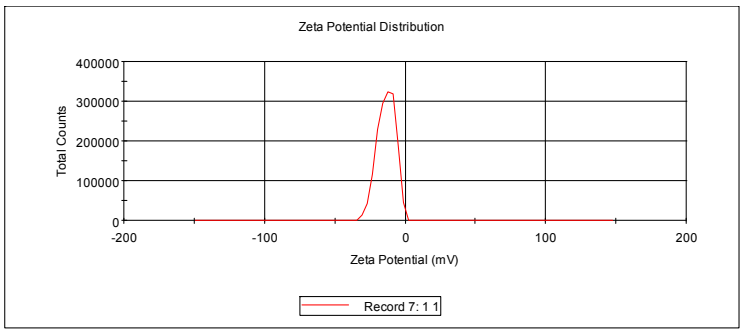

Fig. S5 The zeta potential of GQDs in aqueous solution at pH= 6.5 (Zeta potential value:-13.2mV).

3. Synthesis and Characterization of THPD

THPD was synthesized according to the literature recently reported by our group[3].

3.1 Synthesis of 5,10,15,20-Tetrakis (4-hydroxyphenyl) porphyrin (THPP)

Firstly, 4-hydroxybenzaldehyde (4.9g, 0.04 mol), freshly distilled pyrrole (2.8 mL, 0.04 mol) and propionic acid (100mL) were mixed and refluxing under stirring for 1 hour. Then the solution was filtered and washed with hot water for 5 times. The resulting solid was dried, following by washing using CH_2Cl_2 and ethyl acetate. Further purification was used Methanol/ethyl acetate as gradient elution to pass column chromatography to obtain products. At last, the recrystallization of product was conducted in petroleum ether, and pure purple solid was obtained.^{1}H NMR (400 MHz, DMSO) δ 9.94 (s, 1H), 8.81 (s, 2H), 7.98 (d, 2H), 7.20 (m, 2H), -2.89 (s, 1H). Yield= 6.1%.

3.2 Synthesis of 5,10,15,20-Tetrakis (4-hydroxyphenyl) zinc porphyrin (ZnTHPP)

ZnTHPP was synthesized according to the literature [3,4]. THPP (0.9 g) and zinc acetate ($Zn(CH_3COO)_2$, 2.9 g), was added to CH_2Cl_2 (100 ml) and DMF (100ml) in flask, and the reaction system was vigorously stirred at 60ºC overnight under the nitrogen atmosphere. Then, solvent was evaporated under reduced pressure and the obtained solid was dissolved in a small amount of methanol. The solution was dropwise added into excess deionized water to precipitate, and it was filtered, washed with water for several times and dried to obtain purple solid.^{1}H NMR (400 MHz, DMSO): δ 9.82 (s, 1H), 8.79 (s, 2H), 7.94 (d, 2H), 7.15 (m, 2H). Yield= 95.0 %.

3.3 Synthesis of porphyrin star polymer (THPD)

Polymerization was carried out as follows. In glove box, solution of ZnTHPP (0.2g, 0.176 mmol) and 18-crown-6 ether (0.33 g, 1.25 mmol) in dry distilled THF (10 mL) was added to a 50 mL one-neck flask with potassium hydride (0.056 g, 1.4 mmol) under vigorous stirring conditions for 1hour at 50 ºC. Then DMAEMA (1.6 g, 20.6 mmol) in dry THF (3 mL) was dropwise added in ZnTHPP solution. Then the mixture was heated up to 65 ºC to continue the reaction for 24 hour. The reaction was terminated by deionized water, and the mixture was precipitated in n-hexane for 3 times and then dialyzed against (MWCO: 3500 Da) deionized water for 3 days, finally freeze dried in vacuum to obtain THPD polymers. A certain amount of THPD polymer was added into deionized water to get THPD micelle solutions with required concentration.

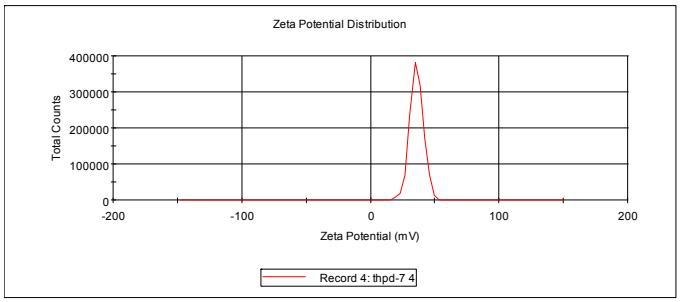

Fig. S6 Zeta potential of THPD unimolecular micelles in aqueous solution with a concentration of 0.04 mg/mL (below CMC).

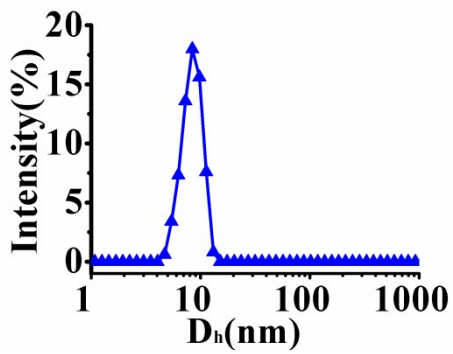

Fig. S7 DLS curve of THPD unimolecular micelles in aqueous solution with a concentration of 0.04 mg/mL (below CMC).

4. Construction of GQDs-THPD light harvesting system

Firstly, THPD aqueous solutions with different concentration was prepared, then a certain amount of these THPD solutions was added into 1mL GQDs solution with concentration of 4.0×10^{-6} M GQDs under vigorously stirring, respectively. The mixed solutions were stirred for 10 min and then left to stand for 30 min.

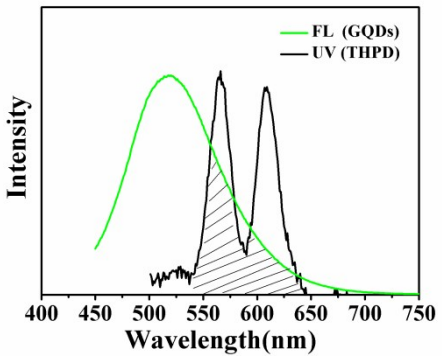

Fig. S8 Normalized fluorescence emission spectra of GQDs (green line) (Ex=410 nm) and absorption spectrum of THPDs (black line).

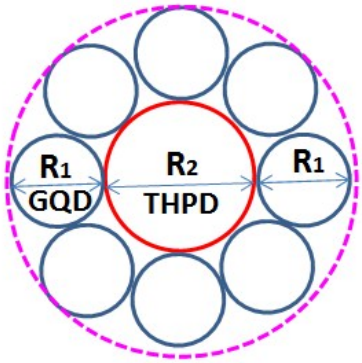

Fig. S9 Geometric scheme of GQDs-THPD LHA. (R_1 is the diameter of GQDs, R_2 is the diameter of THPD, R is the diameter of GQDs-THPD LHA. R_1 = 3.1 nm, R_2 = 5.3 nm, $R=R_1+R_2+R_1$= 11 .5 nm)

5. Light-harvesting properties of GQDs-THPD LHAs

5.1 Calculation of fluorescence quantum yield of GQDs in water

The fluorescence quantum yield of samples in water was determined by using quinine sulfate in 0.05 M H_2SO_4 as a standard according to literatures.[5-6] The quantum yields were calculated with equation(1).

$$\Phi = \Phi_{st}\times(I/I_{st})\times(OD_{st}/OD)\times(\eta^2/\eta_{st}^2) \qquad (1)$$

where Φ is the quantum yield, Φ_{st}= 0.55 for quinine sulfate, I is the integrated area of fluorescence emission peak, η is the refractive index of solvents for sample and standard (when water was used for both systems, $\eta^2=\eta_{1^2}$), and OD is the optical density determined by UV-vis spectroscopy. The subscript "st" refers to the standard sample. In this work, the fluorescence spectra of quinine sulfate were excited at 343 nm. The fluorescence quantum yield of GQDs was calculated to be 9.1 %.

5.2 Calculations of the overlap integral (J) and FRET distance (R_0)

Since the overlap integral J is one of the most significant parameters in FRET, and it can be calculated using following equation(2).

$$J = \int_0^{\infty} f_D(\lambda)\ \xi_A(\lambda)\lambda^4 d\lambda \qquad (2)$$

where λ is the wavelength (in cm) and $\varepsilon_A(\lambda)$ is the molar extinction coefficient of the acceptor (THPD) at wavelength λ, $F_D(\lambda)$ is the fraction of the fluorescence intensity of the donor (GQDs).The overlap integral J is finally calculated to be4.35×10^{13} M^{-1} cm^{-1} nm^4 for fluorescence resonance energy transfer between GQDs and PC.

5.3 Calculation of energy transfer efficiency E of GQDs-THPD complex micelles

FRET efficiencies based on donor quenching with steady-state fluorescence experiments were calculated according to following equation (3).[7]

$$E=1-I_{DA}/I_D \quad (3)$$

where I_{DA} are the intensity of donor's (GQDs) fluorescence emission with and without acceptor (THPD). The excitation wavelength was 410 nm.

Table S1. Light harvesting properties of the LH complexes at different GQDs/THPD ratios.

	Energy transfer efficiency (donor quenching)
D/A：400:1	22.3 %
D/A：400:2	32.9 %
D/A：400:6	47.6 %
D/A：400:8	60.6 %
D/A：400:12	75.5 %
D/A：400:20	93.6 %

5.4 Calculation of antenna effect of GQDs-THPD LHA

Antenna effect was calculated according to equation (4)[8]

$$\text{Antenna effect} = I_{em}\,(\lambda_{ex} = 410\text{ nm})/I_{em}\,(\lambda_{ex} = 426\text{ nm}) \quad (4)$$

where I_{em} (λ_{ex}= 410 nm) is the fluorescence intensity of GQDs-THPD LHAs excited at 410 nm, while I_{em} (λ_{ex} = 426 nm) is the fluorescence intensity of pure THPDs exited at the absorption maxima of THPDs at 426 nm. Both GQDs-THPD LHAs and THPDs have the same THPD concentration.

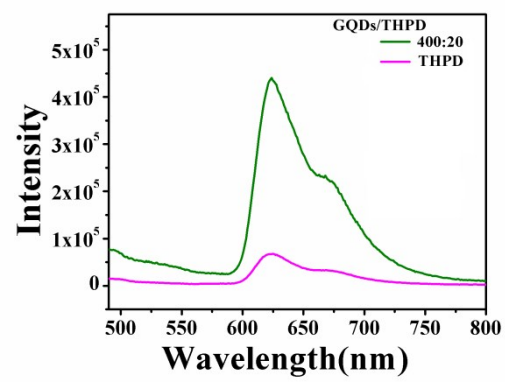

Fig. S10 The fluorescence spectra of GQDs-THPD LHA at the ratio of 20:1 (Ex=410 nm) and of pure THPDs in aqueous solution (Ex=426 nm, the maximum absorption peak of THPD).These two samples have the same concentration of THPDs.

5.5 Calculation of energy transfer rate constant k_{ET}

The energy transfer rate constant was calculated according to equation (5).

$$E=k_{ET}/(k_{ET}+\tau_D^{-1}) \qquad (5)$$

where k_{ET} is energy transfer rate constant, τ_D is the singlet state fluorescence lifetime of GQDs-THPD complex micelles. The k_{ET} between donor and acceptor is calculated to be$5.30 \times 10^9 s^{-1}$.

5.6 Calculation of the distance between donor (GQDs) and acceptor (PC) (R_{D-A})

R_{D-A} is another important parameter in FRET, and it was determined according to equation (6)

$$k_{ET}= 9000\ In10\ k^2\Phi J/(128\pi^5 n^4 N\tau_D R^6) \qquad （6）$$

where k_{ET} is the energy transfer rate constant, k is the orientation parameter ($k^2 = 2/3$ for random orientation), Φ is the fluorescence quantum yield of donor, n is the refractive index of the bulk medium (n = 1.33 in water), N is the Avogadro constant, τ_D is the fluorescence singlet lifetime of donor (GQDs), and R is the center to center distance between donor (GQDs) and acceptor (THPD). The R_{D-A} in this GQDs-THPD light harvesting system was calculated to be about 2.84 nm.

5.7 Calculation of the number of GQDs quenched by THPD

Firstly, nonlinear least-squares fittings of I_F versus the THPD concentration were performed using the following equation 7.[6,9]

$$I_F = I_0 + ((I_{lim}-I_0)/(2\times C_0)) \times(C_0 + C_{TH} + (1/K_a)- ((C_0 + C_{TH} + (1/K_a))\text{^}2-4 \times C_{TH}\times C_0)\text{^}(1/2)) \qquad (7)$$

in which I_F was the observed emission intensity of GQDs-THPD, $I_0$was the emission intensity of GQDs-THPD complex micelles in the absence of THPD, I_{lim} was the emission intensity of the fully complexed GQDs-THPD (zero in the curve fitting), C_0 was the concentration of (GQDs)n, where n is the number of donors quenched by every acceptor. And C_{TH} was the concentration of THPD. This model regarded GQDs as one unit, it combined the directly and indirectly energy-transfer process and it can be expressed as equation 8.

$$(GQDs)n+ THPD = (GQDs)n\times THPD \qquad (8)$$

Through the curve fitting by the software of Matlab, the binding constant（ K_a）was 4.23×10^7 M^{-1} and the concentration of (GQDs)n (C_0) was 2.12×10^{-7} M, since the concentration of GQDs (C_{GQDs}) in this system was about 4.0×10^{-6} M, the number of GQDs that can be quenched by THPD was calculated to be $n=C_{GQDs}/C_0 = 19$.

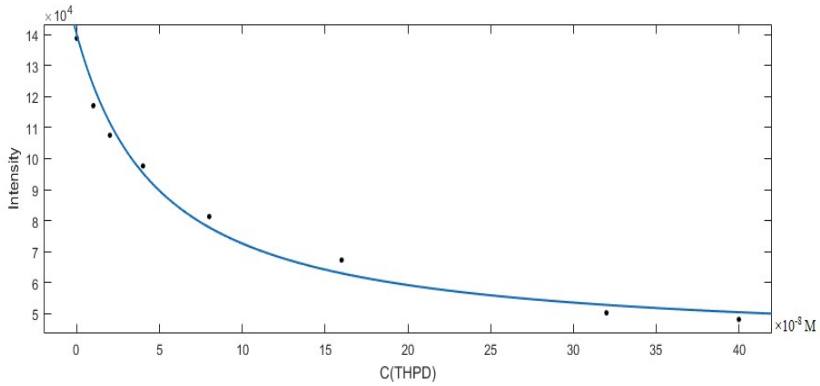

Fig. S11 Nonlinear least-squares fittings of I_F versus the THPD concentration.

References

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