ADVANCED OPTICAL MATERIALS

Supporting Information

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Radiative Rate Modulation Reveals Near-Unity Quantum Yield of Graphene Quantum Dots

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Supporting Information

Radiative rate modulation reveals near-unity quantum yield of graphene quantum dots

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Section S1. Fluorescence correlation spectroscopy measurements

Fluorescence correlation spectroscopy (FCS) allowed us to determine the dimension of GQDs along the vertical axis. From the autocorrelation curves (figure S2) measured with FCS, one obtains the diffusion time τ_D of a particle through the focus (time of decay of the diffusion-related part of the autocorrelation curves to half its maximum value)[1]:

$$\tau_D = \frac{\omega_{xy}^2}{4D} \qquad (1)$$

where D is the diffusion coefficient, and ω_{xy}^2 is the focus width in the xy-plane of the confocal focus. The diffusion coefficient itself is related to the hydrodynamic radius R_H via the Stokes-Einstein relation as:

$$D = \frac{k_B T}{6\pi\eta R_H} \qquad (2)$$

where k_B = 1,3806504 *10^{-23}J/K is Boltzmann's constant and T is the absolute temperature. The particles' hydrodynamic (Stokes) radius R_H is the radius of an equivalent sphere that has the same diffusion coefficient as the given molecule.

Measured diffusion times in aqueous solution at T=293 K were:

for Oregon Green: τ_{OG}= 0.104±0.001 ms

The literature value[2] of the diffusion coefficient for Oregon Green in water at T = 293 K is $4.1 \cdot 10^{-6}$ s*m^2/s. By combining equations (1) and (2), we obtain for the average hydrodynamic radius of the GQDs:

$$R_H = \frac{k_B T \tau_{Cdots}}{6\pi D_{OG} \tau_{OG}} = 0.764 \cdot 10^{-9}\ \text{m} = 0.774\ \text{nm} \quad (3)$$

For non-spherical objects, the hydrodynamic radius is equal to that of a spherical object with same volume times a shape factor f_c (accounting for non-spherical shapes of the solute) which is for oblate spheroids given by[3]

$$f_s = \frac{1}{2} \frac{a\sqrt{\left(\frac{b}{a}\right)^2 - 1}}{arctan\left(\sqrt{\left(\frac{b}{a}\right)^2 - 1}\right)} \quad (4)$$

where a and b represent the extensions of the spheroid along the symmetry axis and the two other axes, respectively ($b/a > 1$ for oblate spheroids).

Section S2. Materials

Alexa 350 was purchased from Thermofisher (Alexa Fluor 350); Atto 390 and Atto 488 dyes were purchased from Atto-Tec. Blue-, cyan- and green-emitting GQDs were purchased from Sigma Aldrich (product numbers 900708, 900707 and 900712, respectively).

Section S3. Confocal microscope

Fluorescence spectra were measured using an Andor SR 303i spectrograph and a CCD camera (Andor iXon DU897 BV). Fluorescence lifetime measurements were performed with a custom-

built confocal microscope equipped with an objective lens of high numerical aperture (Apo N, 60×/1.49 NA oil immersion, Olympus). A white light laser system (Fianium SC400-4-20) with a tunable filter (AOTFnC-400.650-TN) served as excitation source for Atto 488 and Green GQDs. Excitation of Alexa 350, Atto 390, and Blue and Cyan GQDs was performed using a UV laser (Picoquant, LDH-P-C-375). Collected fluorescence was focused onto the active area of a single photon detection module (MPD series, PDM). Data acquisition was accomplished with a multichannel picosecond event timer (PicoQuant HydraHarp 400). Photon arrival times were histogrammed (bin width of 32 ps) for obtaining fluorescence decay curves.

Section S4. Quantum yield measurements of the reference samples using the nanocavity-based method

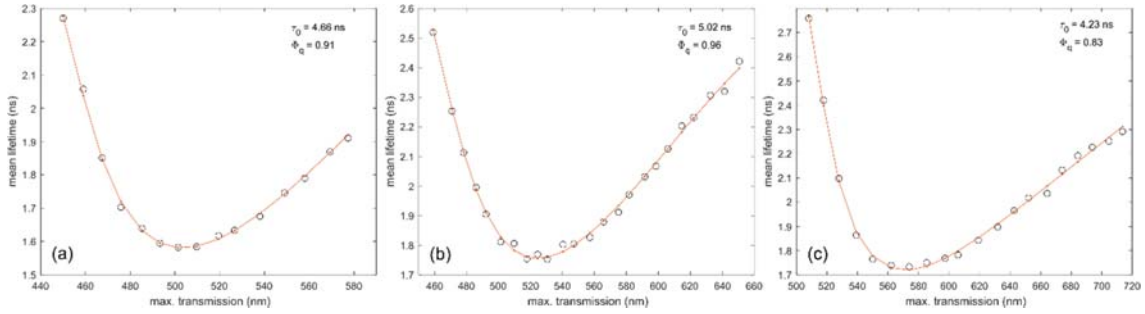

Figure S1. Excited state lifetime of (a) Alexa 350, (b) Atto 390 and (c) Atto 488 as a function of the cavity length. Open black circles are the measured data; the red curve is the fit. The fit parameters are the fluorescence quantum yield and the excited state lifetime in the absence of the cavity.

Section S5. Quantum yield measurement using the comparative method

A standard 10 mm cuvette was used to measured quantum yield (QY) by reference sample method. The concentrations of the samples was chosen in such way that maximum value of absorbance not exceeded 0.1 at excitation wavelength and above, to reduce the re-absorption and other non-linear effect which perturbed the QY values. The measurement protocols are as follows:

(1) Recording of absorption spectra at different concentrations of the sample not exceeded the absorbance of 0.1 at excitation wavelength.

(2) Recording of emission spectra from the same concentrations at which absorption was measured.

(3) Plotting the graph of integrated fluorescence intensity vs. absorbance and fitting with a straightline.

(4) Followed the same for reference samples e.g. dye molecules which have chosen in such a way that absorptions and emissions of dye molecules have at similar wavelength with the unknown samples.

(5) To calculate the QY the following formulae was used:

$$\Phi_{unknown\ sample} = \Phi_{reference} \frac{k_{unknown\ sample}}{k_{reference}} \frac{n_{unknown\ sample}}{n_{reference}} \qquad (5),$$

where Φ is quantum yield *k* is the gradient obtained from integrated fluorescence intensity vs. absorbance plot, *n* is refractive index of the solvent. The corresponding data is shown in Figure S2.

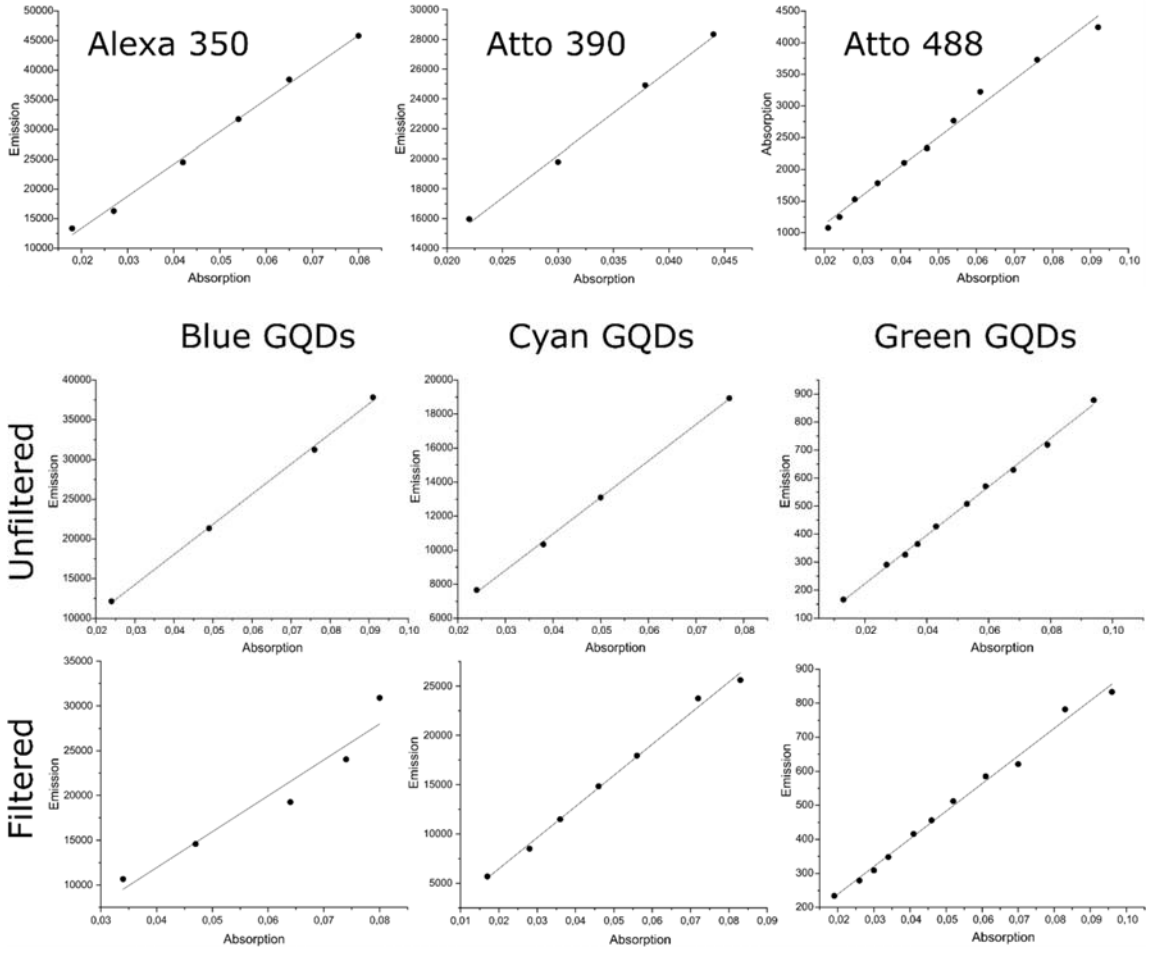

Figure S2. Integrated fluorescence intensity against absorbance for Alexa 350, Atto 390, Atto 488 and blue, cyan and green filtered and unfiltered GQDs.

References

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[2] C. B. Müller, A. Loman, V. Pacheco, F. Koberling, D. Willbold, W. Richtering, J. Enderlein, *EPL (Europhysics Letters)* **2008,** 83, (4), 46001.

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