Singular Wavelength Dependence on the Sensitization of Lanthanides by Graphene Quantum Dots

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Supplementary Information

Methods

Materials were purchased and used without further purification. Anthracite coal was purchased from Fisher-Scientific. Sulfuric Acid (98%) and nitric acid (70%) were purchased from Sigma Aldrich. Terbium chloride hexahydrate, ethylenediaminetetraacetic acid, sodium hydroxide, and sodium borohydride were purchased from Sigma Aldrich. A Krosflo MidiKros was used to filter GDQs by size and all spectral samples were purged with nitrogen for 20 min unless otherwise noted. UV-Vis spectra were taken on a Shimadzu UV-2450 spectrophotometer. Steady state excitation and emission spectra were taken on a Horiba Jobin Yvon NanoLog spectrophotometer. All time resolved emission spectra and decays were taken on an Edinburgh Instruments OB 920 using either a 920H microsecond flash lamp or a EPL375 picosecond pulsed diode laser.

Blue shifted GQD

Graphene quantum dots were synthesized similar to the method previously published.[1] Anthracite coal (2 g) was dispersed in concentrated sulfuric acid (60 mL). Nitric acid (70%, 20 mL) was slowly added to the dispersion. The mixture was heated to 100 °C and allowed to react for 24 h. After cooling to room temperature, the reaction mixture was quenched with NaOH. After filtration through a 0.2 µm mPES membrane, the resulting solution was subjected to cross-flow filtration through 1 and 3 kDa membranes, collecting the fraction retained by the 1 kDa membrane and that passes through 3 kDa. GQDs were isolated via rotary evaporation of the solvent. A 1 mg/mL solution of GQDs (20 mL) in 0.5 M NaOH was added to a Teflon-lined stainless-steel autoclave and was heated to 200 °C for 24 h. After cooling to room temperature, sodium borohydride was added, and the solution was stirred for 8 h at room temperature. Following dialysis (1 kDa membrane), blue-shifted GQDs were obtained after rotary evaporation.

Red shifted GQD

Graphene quantum dots were synthesized similar to the method previously published.[1] Anthracite coal (2 g) was dispersed in concentrated sulfuric acid (60 mL). Nitric acid (70%, 20 mL) was slowly added to the dispersion. The mixture was heated to 100 °C and allowed to react for 24 h. After cooling to room temperature, the reaction mixture was quenched with NaOH. After filtration through a 0.2 µm mPES membrane, the resulting solution was subjected to cross-flow filtration against a 70 kDa membrane. The redder-emitting GQDs were isolated via rotary evaporation from the fraction retained by the 70 kDa membrane.

Spectroscopic characterization

To measure the sensitization of Tb^{3+}, nine solutions of bGQDs (5 µg/mL) in water were made with increasing amounts of $TbCl_3$ (0-50 µM). Solutions were purged with nitrogen, then emission spectra measured using the same instrument parameters. The spectra were processed using OriginPro 8.5. The broad emission from the GQD was marked as a baseline and the Tb^{3+} peak centered at 545 nm was integrated. This peak was used because it was visible at all concentrations other than 0 µM Tb^{3+}. The peak area was then plotted verses concentration of $TbCl_3$ to determine the optimal concentration.
The average lifetime was calculated from the multiexponential decay using the following equations given a tri-exponential fit.

$$y = y_0 + A_1 e^{\left(-x/\tau_1\right)} + A_2 e^{\left(-x/\tau_2\right)} + A_3 e^{\left(-x/\tau_3\right)}$$

$$P_n = \tau_n * \left(\frac{\tau_n A_n}{\tau_1 A_1 + \tau_2 A_2 + \tau_3 A_3}\right)$$

$$\tau_{avg} = \tau_1 P_1 * \tau_2 P_2 * \tau_3 P_3$$

The quantum yield (QY) of bGQD was measured using nitrogen purged $[Re(bpy)(py)(CO)_3]^+$ aqueous solutions as a reference; given that the QY of $[Re(bpy)(py)(CO)_3]^+$ is 0.015, bGQD was found to have a quantum yield of 0.094 following equation.

$$\Phi = \Phi_R\left(\frac{Int}{Int_R}\right)\left(\frac{\eta^2}{\eta_R^2}\right)$$

This was also used to measure the quantum yield of Tb@bGQD, rGQD, and Tb@rGQD. For Tb@bGQD and Tb@rGQD, emission spectra were processed with OriginPro 8.5. The total area was integrated, then the broad GQD emission was marked as a baseline and the area of the four Tb^{3+} peaks were integrated and used for Φ_{Tb}. The area of Tb^{3+} was then subtracted from the total area and the result was used to determine Φ_{GQD}. Once the quantum yield was determined at 250 nm it could be used to determine the QY over all excitation wavelengths. The ratio of PL area /Abs of the 3D spectra was determined at 250 nm, then that coefficient was applied to the PL area /Abs ratio at each excitation wavelength.

Singlet oxygen was detected using a single grating spectrometer equipped with a liquid-N2 cooled InGaAs array detector. Samples were prepared in D_2O so that they had an absorption of 0.2 at 365 nm. The phenalenone standard and one bGQD sample were purged with oxygen for 15 min and sealed with parafilm, the other bGQD sample was purged with nitrogen. Samples were excited at 365 nm and spectra were measured 1210 – 1325 nm.

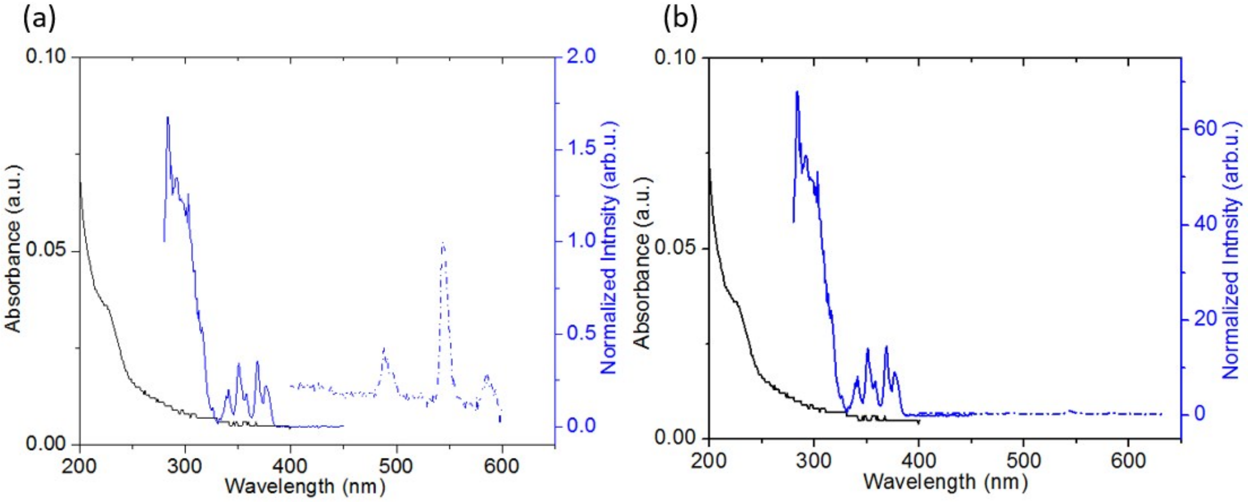

Figure S1. Absorption (black), excitation (blue solid) and emission (blue dashed) spectra of $TbCl_3$ excited at (a) 280 nm and (b) 330 nm.

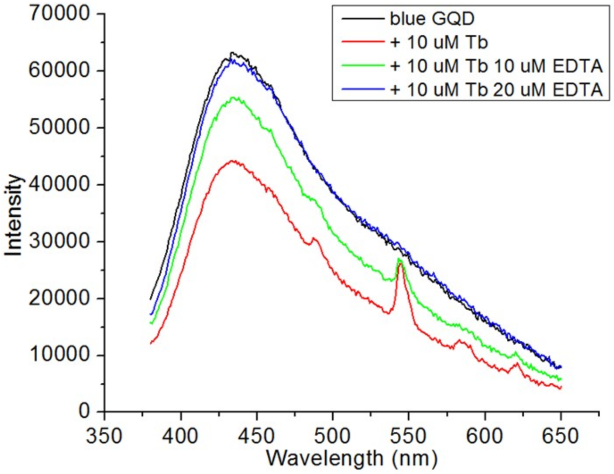

Figure S2. Sequestering of Tb^{3+} with two equivalents of EDTA. bGQD (5 µg/mL) was purged with nitrogen and excited at 330 nm. To that sample Tb^{3+} (10 µM) was added, purged again and excited at 330 nm. Then equivalents of EDTA were subsequently added with purging and measurement taken until the PL spectra of the bGQD was recovered.

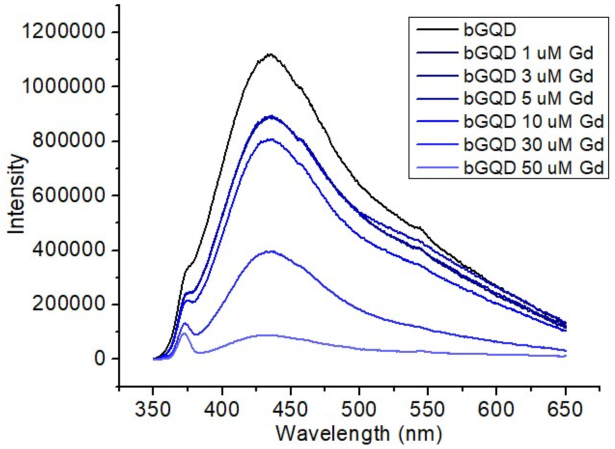

Figure S3. Titration of Gd@bGQD. Quenching of emission intensity is seen with increased concentration of $GdCl_3$. Each sample of bGQD (5 µg/mL) and Gd^{3+} (0-50 µM) was purged with nitrogen and excited at 330 nm.

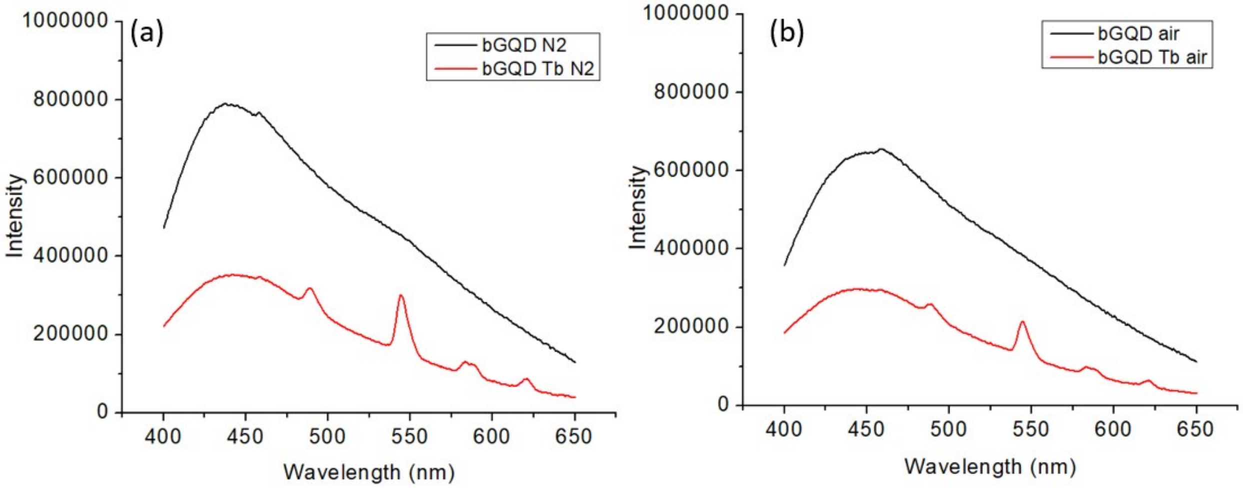

Figure S4. Photoluminescence bGQD and Tb@bGQD (a) purged with nitrogen and (b) open to air. $[Tb^{3+}]$ = 10 µM and [bGQD] = 5 µg/mL. Excited at 330 nm.

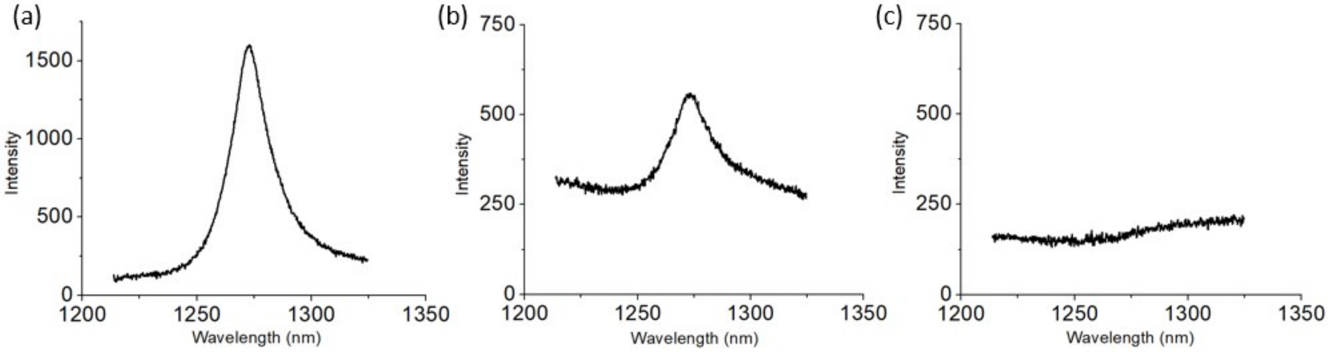

Figure S5. Near IR emission spectra showing singlet oxygen generation of (a) phenalenone standard, (b) bGQDs purged with oxygen, and (c) the absence in bGQD purged with nitrogen. Excited at 365 nm with 800 nm filter.

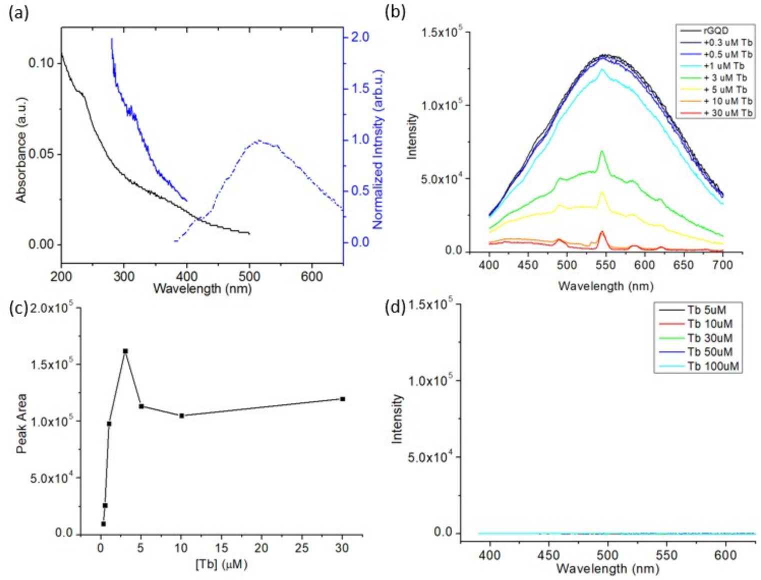

Figure S6. (a) Absorption (black), excitation (blue solid) and emission (blue dashed) spectra of rGQDs (5 μg/mL) in water excited at 330 nm. (b) Emission spectra of $TbCl_3$ titration into aqueous solution of rGQDs. (c) Plot of emission intensity recorded at 545 nm from (b) the $TbCl_3$ titration. (d) Photoluminescence of $TbCl_3$ at varying concentrations in water excited at 330 nm.

Table S1. Photophysical parameters for rGQD and Tb@rGQD.

Sample	ϕ_{Tb}	ϕ_{GQD}	$\tau_{520\ nm}$	$\tau_{545\ nm}$
rGQD	-	0.018	0.42 ns (15%)	-
	-	-	2.01 ns (47%)	-
	-	-	6.74 ns (38%)	-
Tb@rGQD	0.00016	0.0075	0.38 ns (22%)	553 μs
	-	-	1.84 ns (45%)	-
	-	-	6.97 ns (33%)	-

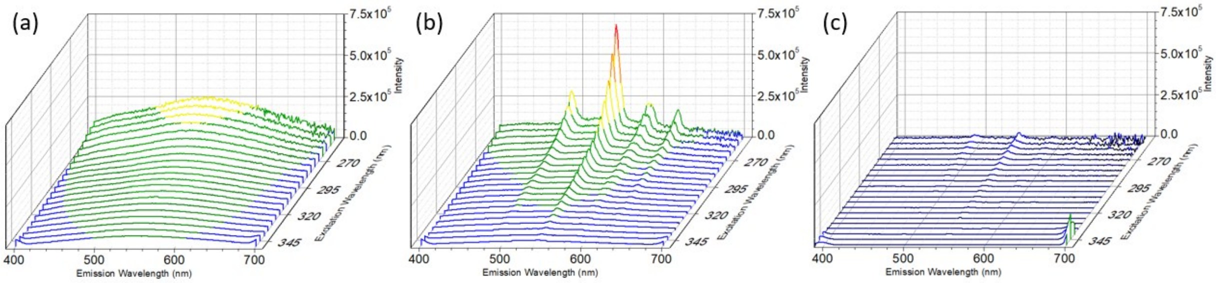

Figure S7. 3D emission spectra of (a) rGQD (10 μg/mL) (b) Tb@rGQD (6 μM and 10 μg/mL) and (c) $TbCl_3$ (6 μM) purged with nitrogen.

References

1) R. Ye, C. Xiang, J. Lin, Z. Peng, K. Huang, Z. Yan, N. P. Cook, E. L. Samuel, C.-C. Hwang, G. Ruan, G. Ceriotti, A.-R. O. Raji, A. A. Martí, and J. M. Tour, *Nat. Commun*., 2013, **4**, 3943.