

## Supporting Information

### **Charge Transfer in Graphene Quantum Dots Coupled with Tetrathiafulvalenes**

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## **Experimental Section**

### **1. Materials and methods**

The graphite used for the production of graphene oxide (GO) was purchased from TIMCAL (TIMREX SFG15,  $\rho = 2.26 \text{ g}\cdot\text{cm}^{-3}$ , particle size = 8.80  $\mu\text{m}$ , surface area = 9.50  $\text{m}^2\cdot\text{g}^{-1}$  ash  $\leq 0.100\%$ , interlaminar distance = 0.3354–0.3358 nm). 2-hydroxymethyl-9,10-bis-(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene was synthesized by following the previously reported method.<sup>1</sup>

All other reagents were purchased from commercial sources and used without further purification unless otherwise stated. Thin-layer chromatography was performed on Merck silica gel 60 F254 plates; chromatograms were visualized with UV light (254 and 360 nm). Vacuum filtrations of nanomaterials were carried out with polytetrafluoroethylene (PTFE) membranes.

### **2. Instruments**

**TEM** micrographs were obtained using a JEOL 2100 microscope operating at 200 kV. The samples were dispersed in EtOH and dropped onto a holey carbon copper grid (200 mesh), the solvent was removed in a vacuum oven during 48 h. **AFM** was performed under ambient conditions using SPM Nanoscope IIIa multimode working on tapping mode with a RTESPA tip (Veeco) at a working frequency of B235 KHz. Height and phase images were simultaneously obtained. The samples were prepared by drop-casting or spin coating on freshly cleaved mica from EtOH suspensions and were dried under ambient conditions for 24 hours and later in a vacuum oven during 48 hours. **TGA** analyses were carried out under nitrogen in a TA-TGA-Q500 apparatus. The sample (~ 0.5 mg) was introduced inside a platinum crucible and equilibrated at 100 °C followed by a 10 °C  $\text{min}^{-1}$  ramp between 100 and 1000 °C followed by an isotherm of 30 minutes. **FTIR** spectra were carried out in a Bruker TENSOR 27 using a spectral range of 4000–400  $\text{cm}^{-1}$ , with a resolution of 1  $\text{cm}^{-1}$ , and in pellets of dispersed samples of the corresponding materials in dried KBr. **Raman** spectra were recorded on a NT-MDT-in Via Microscope at room temperature using an exciting laser source of 532 nm. **Cyclic Voltammetry** experiments were carried out on a potentiostat/galvanostat AUTOLAB with PGSTAT30 equipped with a software GPES for

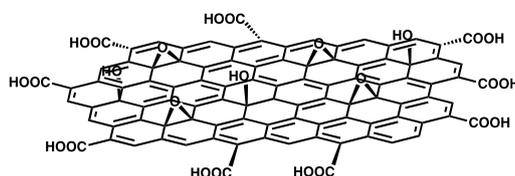
windows version 4.8 in a conventional three compartment cell. Measurements were carried out using a GCE (glassy carbon) as working electrode, a Ag/AgNO<sub>3</sub> reference electrode, and a Pt wire as counter electrode. *n*Bu<sub>4</sub>PF<sub>6</sub> was used as supporting electrolyte and DMSO as solvent. **UV-Vis** spectra were recorded with a Shimadzu Spectrophotometer UV-3600 at 25 °C, with a resolution of 1 nm.

A Horiba Jobin Yvon Fluoromax 3 spectrometer was used for the **steady state fluorescence** measurements. By recording the S/R-channel the fluorescence spectra are corrected with respect to the lamp spectrum. The integration time was set to 0.1 s, while the entrance and exit slits of excitation and emission monochromator were set to 2 nm. All measurements were performed in 10 x 10 mm quartz cuvettes. The software FluorEscence was used for data evaluation.

For **femtosecond transient absorption spectroscopy**, Clark MXR fs-laser systems CPA 2101 as well as CPA 2110 were used combined with an optical detection system from Ultrafast Systems LLC. The laser source was a Ti:sapphire laser with an excitation wavelength of 775 nm, a pulse width of 150 fs, and a frequency of 1 kHz. The SHG provided the excitation wavelength of 387 nm. The samples were measured in a 2 mm quartz cuvette. The software Surface Explore Pro from Ultrafast Systems was used for data evaluation. A multi-wavelength analysis was performed using the software Glotaran.<sup>2</sup>

### 3. Synthetic details and characterization

#### Synthesis of GO by Kovtyukhova-Hummer's method



The modified Hummer's method reported by Kovtyukhova *et al.*<sup>3</sup> was adapted with some modifications.<sup>4</sup> The steps involved in the preparation of GO are described in detail below.

*Pre-oxidation of graphite:* graphite powder (4 g),  $K_2S_2O_8$  powder (2 g), and  $P_2O_5$  (2 g) were dry-mixed in a 250 mL round bottom flask followed by the addition of sulfuric acid ( $H_2SO_4$ , 98%, 10 mL). The mixture was refluxed at 80 °C for 6 hours. The mixture was left to cool down to room temperature and then diluted in 250 mL of deionized water. The mixture was filtered over a hydrophilic PTFE membrane (0.1  $\mu m$ ) and washed with water until the filtrate became neutral. The filter cake obtained was oven dried at 50 °C overnight affording a black-grey powder.

*Low temperature stage:* The dried pre- oxidized graphite powder (~ 4 g) and  $NaNO_3$  (4 g) were dry-mixed in a 500 mL round bottom flask. Then  $H_2SO_4$  (98%, 100 mL) was added and the mixture was kept stirring at 0 °C on an ice bath. When the powders were fully dispersed,  $KMnO_4$  (12 g) was added slowly to the suspension. The addition rate was carefully controlled so that the temperature of the suspension was kept below 20 °C. After the addition of  $KMnO_4$  was complete, the suspension was stirred at 0 °C for an additional 10 minutes.

*Medium temperature stage:* The ice bath was removed and the temperature was raised to 35 °C. The resulting mixture was allowed to stir at this temperature for 2 hours. Afterwards, the brown pasty suspension was heated to 60 °C.

*High temperature stage:* Once the temperature reached 60 °C, 50 mL of deionized water was added to the mixture and stirred for 5 minutes. After this time, the temperature was set to 80 °C followed by the addition of 80 mL of deionized water and  $H_2O_2$  (35 %, 10 mL).

The mixture was stirred for 30 minutes at 80 °C and then cooled to room temperature and stirred until the next day, where it was obtained a brown pasty mixture.

*Washing and purification:* The brown suspension obtained in the previous step was filtered over a hydrophilic PTFE membrane (0.1 μm) and washed with an aqueous solution of HCl (1N) until the collected filtrate solution becomes nearly transparent. Afterwards, the brown solid was washed with an aqueous solution NaOH (1N) and the collected filtrate solution becomes dark brown. Finally, the solid was resuspended in deionized water, sonicated for 1 hour and centrifuged at 3000 rpm for 5 minutes. The obtained black solid was dried in an oven at 60 °C for one week (5 g).

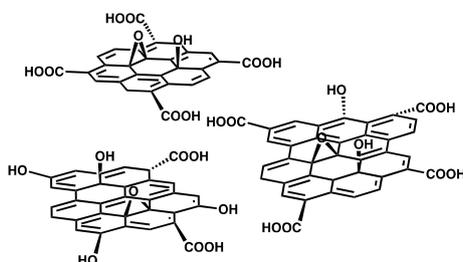
FTIR (KBr),  $\nu$  (cm<sup>-1</sup>): 1719 (C=O stretching mode) and 1561 (C=C stretching mode).

TGA (N<sub>2</sub> atmosphere): weight loss and temperature desorption (organic anchoring groups): 36%, 650 °C.

UV-Vis (H<sub>2</sub>O),  $\lambda_{\max}$  (nm): 240.

XPS: % atomic: C (284.4 eV) = 70.1, O (532.3 eV) = 29.9.

### Synthesis of GQD



The GO (5 g) obtained by the Kovtyukhova-Hummer's method was added over a mixture of concentrated H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> (3/1, v/v, 250 mL). The solution was subjected to ultrasonic treatment for 3 hours and then stirred at 120 °C for 24 hours. After this period of time, the mixture was cooled to room temperature and filtered over a hydrophilic PTFE membrane (0.1 μm). The collected filtrate was diluted with deionized water and neutralized with a saturated potassium carbonate solution. Water was removed under reduced pressure until a final volume of around 100 mL was reached. This solution was subjected to dialysis

(bags of 2000 Daltons) for one week. Finally, water was removed under reduced pressure to afford GQD (265 mg).

FTIR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 1719 (C=O stretching mode), 1611 (C=C stretching mode) and 1150 (C-O stretching mode).

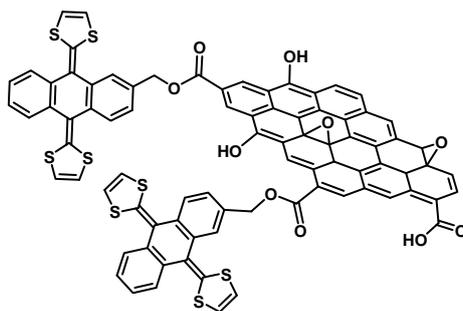
TGA ( $\text{N}_2$  atmosphere): weight loss and temperature desorption (organic anchoring groups): 38 %, 650 °C

Raman, shift ( $\text{cm}^{-1}$ ): 1600 (G band), 1390 (D band).  $I_D/I_G = 0.92$ .

UV-Vis ( $\text{H}_2\text{O}$ ),  $\lambda_{\text{max}}$  (nm): 225 ( $\pi-\pi^*$ ), 270 ( $n-\pi^*$ ).

XPS: % atomic: C (284.6 eV) = 70.5, O (532.4 eV) = 29.4.

### Synthesis of GQD-exTTF



GQD (60 mg) were refluxed in  $\text{SOCl}_2$  (10 mL) for 24 hours at 70 °C under argon atmosphere, the excess of  $\text{SOCl}_2$  was then evaporated using argon as carrier gas. The GQD modified with acid chlorides were reacted *in situ* with 2-hydroxymethyl-exTTF<sup>1</sup> (60 mg), dissolved in 3.0 mL of DMSO, at 110 °C for 24 hours and under argon atmosphere. The resulting mixture was added over cold diethyl ether and was centrifuged at 6000 rpm for 10 min. Afterwards, the ether solution was removed and fresh cold ether was added and the mixture centrifuged again in the same conditions. This process was repeated several times until the ether solution was colourless. The black solid was suspended in dichloromethane (DCM) and separated by filtration through a 0.1  $\mu\text{m}$  hydrophilic PTFE membrane and subjected to consecutive washings with DCM, MeOH and water until the collected solution was colourless. The obtained black powder was dried in vacuum to obtain a dark brown solid (26 mg).

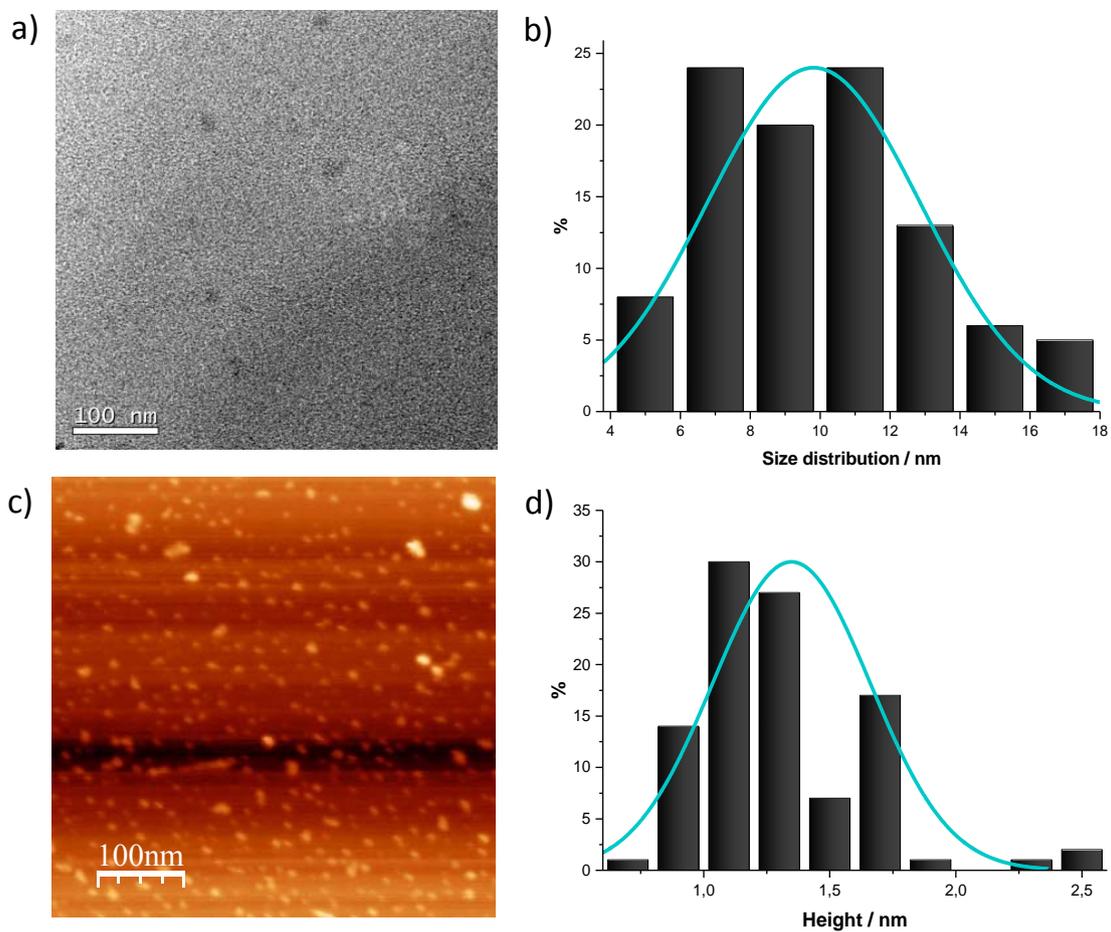
FTIR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 1732 (C=O stretching mode), 1719 (C=O stretching mode), 1611 (C=C stretching mode) and 645 (C-S stretching mode).

TGA ( $\text{N}_2$  atmosphere): weight loss and temperature desorption (organic anchoring groups): 66 %, 650 °C

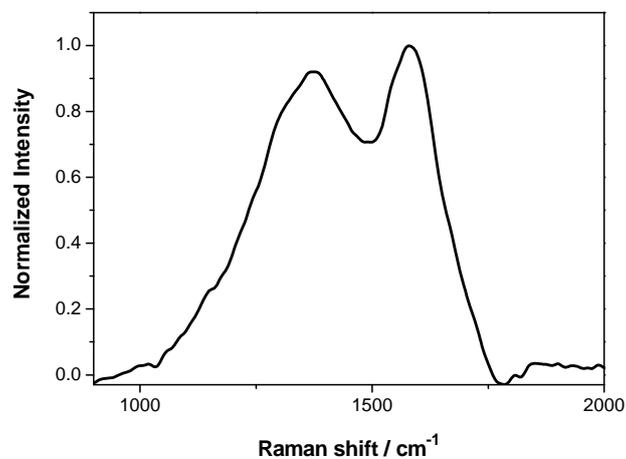
Raman, shift ( $\text{cm}^{-1}$ ): 1571 (G band), 1345 (D band).  $I_D/I_G = 1.00$ .

UV-Vis (DMSO),  $\lambda_{\text{max}}$  (nm): 367, 432.

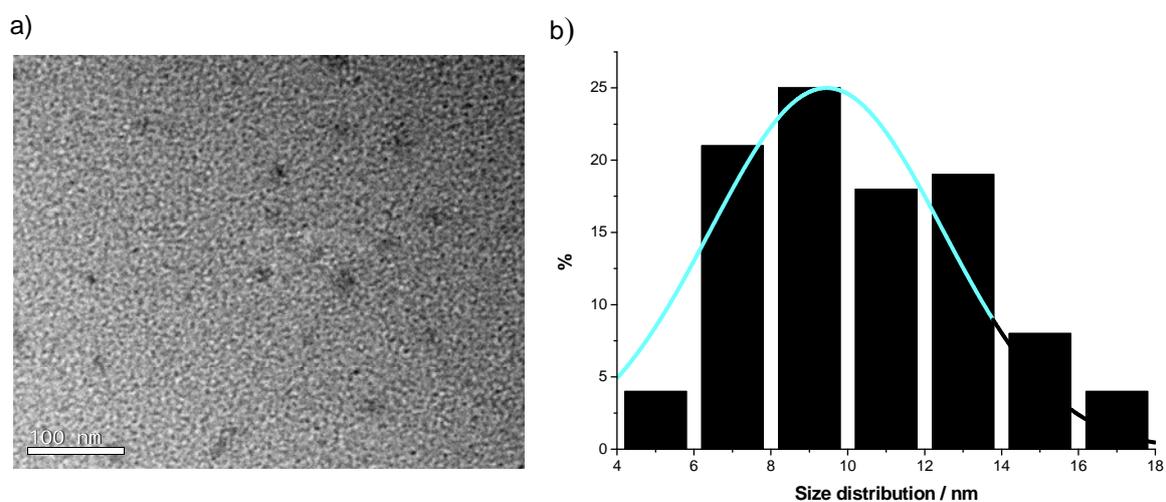
XPS: % atomic: C (284.6 eV) = 69.0, O (531.6 eV) = 25.1, S (163.6 eV) = 5.9.



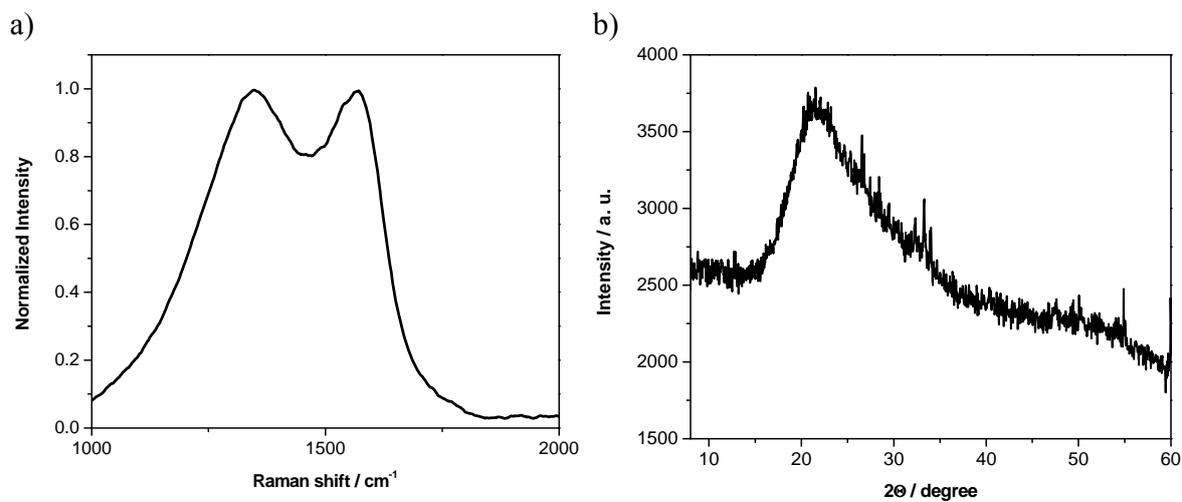
**Figure S1.** a) Representative TEM image of GQD. b) Size histogram with a curve fit of the data using a Gaussian model. Average size:  $10.0 \pm 3.1$  nm. c) Representative AFM image of GQD. d) Height histogram with a curve fit of the data using a Gaussian model. Average height:  $1.3 \pm 0.3$  nm.



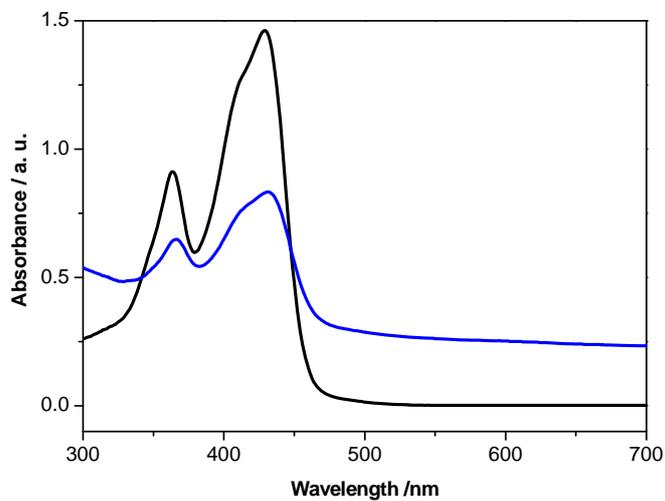
**Figure S2.** Raman spectra of GQD recorded at room temperature and with a laser excitation wavelength of 532 nm.



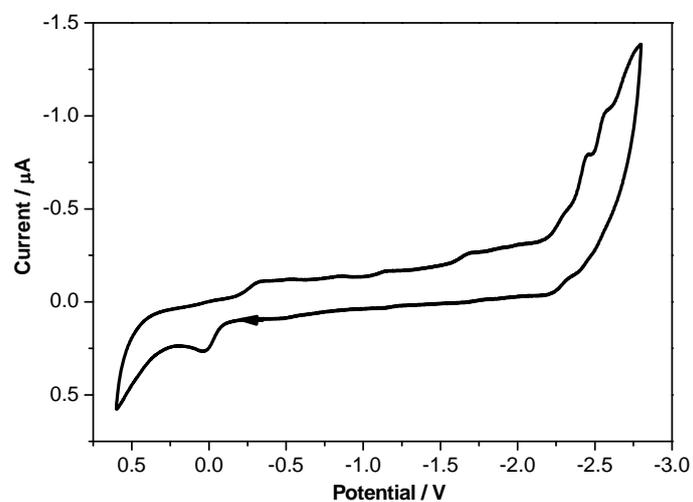
**Figure S3.** a) Representative TEM image of GQD. b) Size histogram with a curve fit of the data using a Gaussian model. Average size:  $9.4 \pm 3.0$  nm.



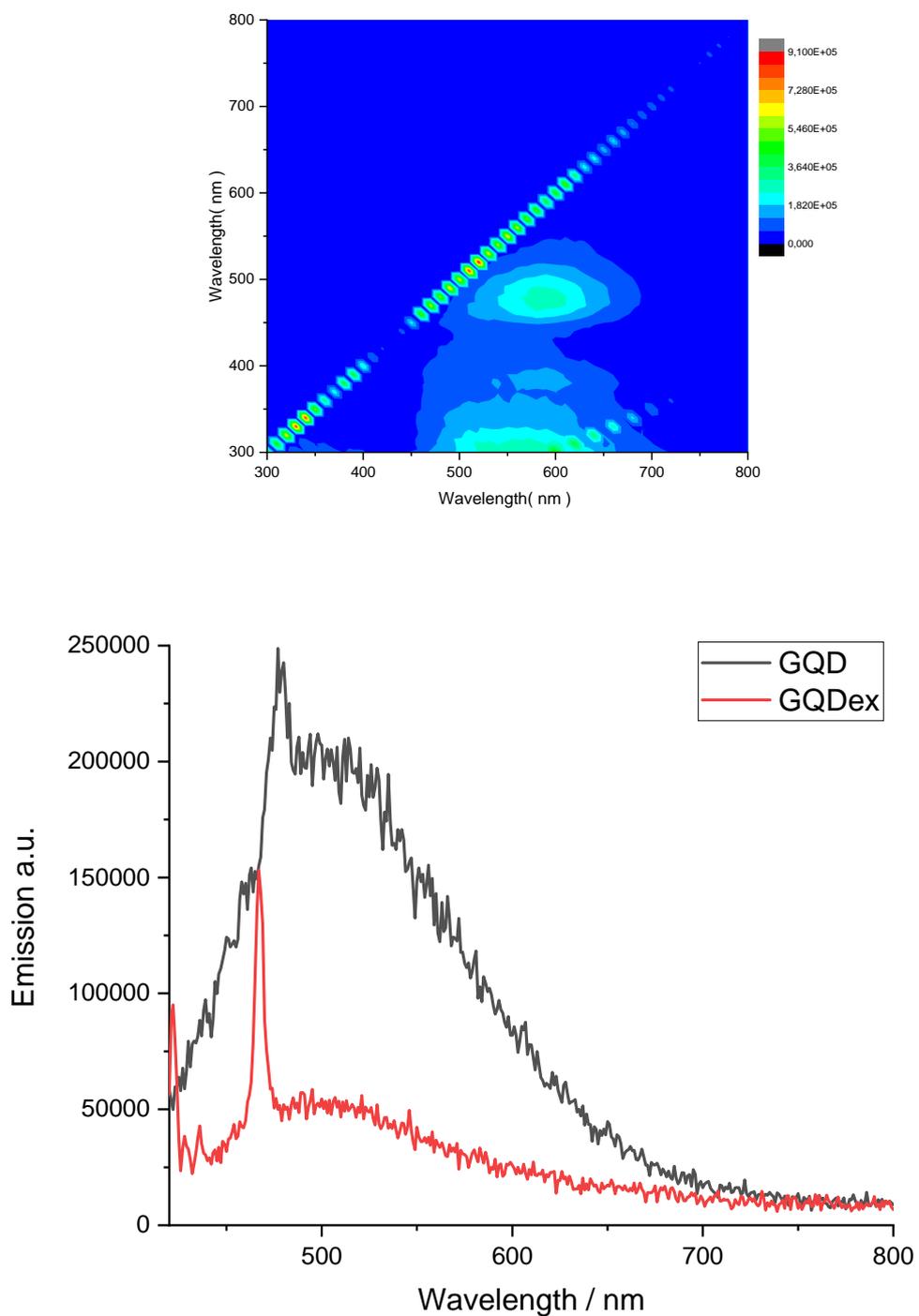
**Figure S4.** a) Raman spectra of GQD recorded at room temperature and with a laser excitation wavelength of 532 nm. b) Powder XRD pattern of **GQD-exTTF**.



**Figure S5.** UV-Vis absorption spectra of a reference exTTF (black) and **GQD-exTTF** (blue) in DMSO solutions.



**Figure S6.** Cyclic voltammogram of **GQD-exTTF** in a DMSO solution containing 0.1M  $n\text{Bu}_4\text{PF}_6$  as supporting electrolyte. Glassy carbon was used as working electrode,  $\text{Ag}/\text{AgNO}_3$  as reference electrode, and a Pt wire as counter electrode.



**Figure S7.** Top: 3D-emission map of GQD-exTTF. Bottom: Steady state emission spectra of GQD (black) and **GQD-exTTF** (red) obtained at an excitation of 410 nm in DMSO.

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<sup>1</sup> G. J. Marshallsay and M. R. Bryce, *J. Org. Chem.*, 1994, **59**, 6847.

<sup>2</sup> J. J. Snellenburg, S. P. Laptanok, R. Seger, K. M. Mullen, I. H. M. van Stokkum, *J. Stat. Soft.* 2012, **49**, 1.

<sup>3</sup> N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva and A. D. Gorchinskiy, *Chem. Mater.*, 1999, **11**, 771.

<sup>4</sup> K.-C. Mei, N. Rubio, P. M. Costa, H. Kafa, V. Abbate, F. Festy, S. S. Bansal, R. C. Hidera and K. T. Al-Jamal, *Chem. Commun.*, 2015, **51**, 14981.