

Enhancing Charge Transfer Efficiency in Graphene Quantum Dots Coupled with Tetrathiafulvalenes

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Tobias Scharl,^c Andrés Ferrer-Ruiz,^a Adrián Saura-Sanmartín,^a Laura-Rodríguez-Pérez,^a M. Ángeles Herranz,^{*a} Nazario Martín,^{*ab} Dirk M. Guldi^{*c}

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Water soluble fluorescent graphene quantum dots have been successfully prepared through a top down approach, that is, starting with graphite, and covalently functionalized with π -extended tetrathiafulvalene. Charge transfer investigations reveal a noticeably slower charge recombination when compared with exTTF nanoconjugates featuring carbon nanodots, for which a larger presence of trap states is observed.

Photoluminescent carbon nanomaterials, carbon nanodots (CND), and graphene quantum dots (GQD), have triggered an increasing attention over the last decade owing to their low-cost production methods, good photostability, low toxicity and chemical inertness.¹ These nanocarbons are versatile nanotools for a wide range of applications including novel energy conversion and storage schemes or photocatalytic fuel production systems.²

The structures of CND and GQD are quite different and so are their properties, even when both terms have been loosely used and interchanged in many different ways.³ CND are mainly prepared by bottom-up synthetic strategies and are best described as amorphous, quasi-spherical nanoparticles that have molecular-like excited states and consequently do not display quantum confinement effects.⁴ On the contrary, GQD are typically obtained from graphene or graphite by top-down approaches and consist of small fragments of few-layer graphene sheets, which leads to two-dimensional disc-shaped structures.⁵

The versatility of CND in charge-transfer assays has been investigated at several occasions. Importantly, the complex electronic structure of CND allows them to act as electron donors or acceptors.⁶ For example, when assembled with perylene diimides (PDI)⁷ or single-walled carbon nanotubes (SWCNT),⁸ CND seem to donate electrons upon photoexcitation. In stark contrast, when combined with

porphyrin⁹ or tetrathiafulvalene¹⁰ derivatives, the CND behave as electron-acceptors. Furthermore, the different composition of CND, and the chemical linkage between CND and the aforementioned electroactive units – by means of covalent or non-covalent approaches – has a notable impact on the charge separation and charge recombination dynamics.⁹ In general, in ultrafast processes, visible-light excitation transforms the singlet excited states into short-lived charge-separated states, which decay between tens and hundreds of ps.

GQD have received much less attention in electron donor-acceptor systems. Reported examples of functionalized GQD have mainly considered the improvement of their emission,¹¹ the development of composite¹² or chiral materials,¹³ and the preparation of self-assembled nanomaterials¹⁴ or supramolecular polymers.¹⁵

Herein, we decided to explore the synthesis of electron-donor acceptor systems based on GQD and the electron donating π -extended tetrathiafulvalene units (exTTF).¹⁶ Following our previous work on covalently linked CND-exTTF nanoconjugates,¹⁰ we focused in the preparation of **GQD-exTTF** analogous, to investigate the structural differences between CND and GQD nanomaterials and how their differences might influence the charge-transfer dynamics in excited state events.

The production of GQD has been carried out from graphene oxide (GO) obtained by the Kovtyukhova-Hummer's method¹⁷ and subsequent oxidative cutting in a mixture of concentrated H₂SO₄/HNO₃, followed by neutralization of the excess of acid, and dialysis similar to that reported by Haino.¹¹ First insights in the morphology of the as-prepared GQD were obtained from transmission electron microscopy (TEM) and atomic force microscopy measurements (AFM). Here we were able to confirm the presence of a mixture of isolated and few-layered GQD with sizes in the range from 4 to 18 nm and 1.3 ± 0.3 nm heights (Fig. S1). With the aim of obtaining additional structural information, Fourier transform infrared (FTIR) and Raman spectroscopies were performed. In the FTIR, the stretching vibrations of the OH, C=O and C-O bonds were found at 3450, 1719 and 1382-1103 cm⁻¹, in addition to the skeletal in-plane vibration of the C=C bonds at 1611 cm⁻¹. The latter confirms that GQD retain the sp² lattice of pristine graphite (Fig. 1). Furthermore, the Raman spectrum shows the

^a Department of Organic Chemistry, Faculty of Chemistry, Complutense University of Madrid, Avda. Complutense s/n, Ciudad Universitaria, E-28040 Madrid, Spain. E-mail: maherran@ucm.es, nazmar@ucm.es

^b IMDEA-Nanociencia, c/Faraday 9, Campus Cantoblanco, 28049 Madrid, Spain

^c Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials (ICMM), Friedrich-Alexander Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany. E-mail: dirk.guldi@fau.de

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characteristic G-band at 1600 cm^{-1} related to the vibration of the sp^2 carbons backbone and also an intense D-band at 1390 cm^{-1} . Considering a I_D/I_G ratio of 0.92 we infer the success in oxidative cutting and introduction of sp^3 -defects in GQD structure (Fig. S2).

In the next step, we activated the carboxylic acids, which are present in GQD, via acid chloride formation and subsequent esterification reaction with 2-hydroxymethyl-exTTF¹⁸ to yield the **GQD-exTTF** nanoconjugates (Scheme 1).



Scheme 1 Schematic representation of the **GQD-exTTF** synthesis.

AFM measurements provided information about the sizes and dimensions of the **GQD-exTTF** nanoconjugates. Overall, the images revealed roundish morphologies with average sizes of $4.6 \pm 1.6\text{ nm}$, which are higher than those seen in the as-prepared GQD, although several agglomerated morphologies are observed (Fig. 1). No significant changes after the functionalization were observed in the GQD core by Raman spectroscopy, where the characteristic D- and G-bands are observed, or by XRD, which presents a typical amorphous graphitic pattern (Fig. S3).

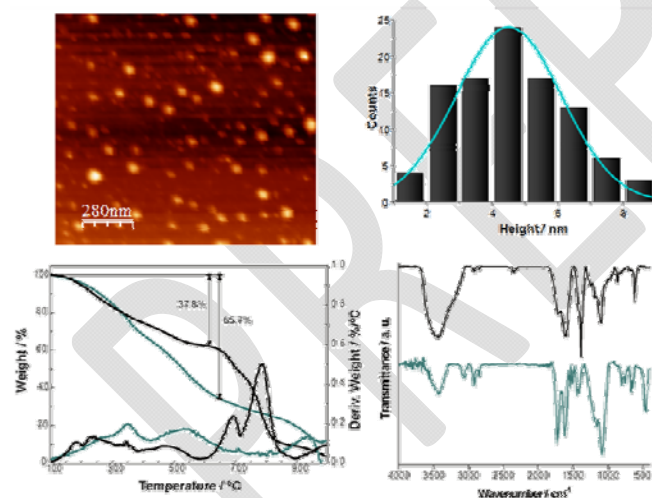


Fig. 1 Top: tapping mode AFM image of **GQD-exTTF** on a mica substrate and height profile histogram with a curve fit of the data using a Gaussian model. Average size: $4.6 \pm 1.6\text{ nm}$. Bottom (left): TGA and first derivative under inert condition of GQD (black) and **GQD-exTTF** (dark cyan). Bottom right: FTIR spectra of GQD (black) and **GQD-exTTF** (dark cyan).

The first evidence of covalent functionalization was gathered from thermogravimetric analysis (TGA) under inert atmosphere (Fig. 1). Up to 650 °C , when the decomposition of GQD starts, a weight loss of around a 66% is observed for **GQD-exTTF** vs. the as-prepared GQD, which experienced a 38% loss at this temperature. The 28% weight loss difference is

assigned to the thermal cleavage of the exTTF. In addition, FTIR spectroscopy offers evidence for the new functional groups, which were introduced on GQD. The C-S stretching vibrations were noted at 645 cm^{-1} with albeit lower intensity. Moreover, it is worth to point out the presence of the C=O stretching vibration at 1740 cm^{-1} as part of the newly formed ester groups.

X-ray photoelectron spectroscopy (XPS) was valuable to gain structural information about **GQD-exTTF**. XPS survey spectrum reveals the presence of oxygen, carbon, and, more interestingly, sulphur at 531.6, 284.6, and 163.6 eV, respectively (Fig. 2). The C 1s band was deconvoluted using six components. To this end, a major component at 284.1 eV due to C=C/C-C bonds is complemented by four minor components at higher binding energies stemming from carbon atoms bound to oxygen in different configurations: 284.8 eV (C-O), 285.7 eV (C-O-C), 286.2 eV (C=O) and 287.9 eV (O-C=O). The last component at about 291.0 eV corresponds to $\pi-\pi^*$ bonds.¹⁹ The XPS S 2p band measured at 163.6 eV is characteristic for C-S-C in tetrathiafulvalene (TTF) derivatives.²⁰ The distinctive absorptions of exTTF were evident in the absorption spectrum of **GQD-exTTF**, as two maxima at 367 and 432 nm (Fig. S5).

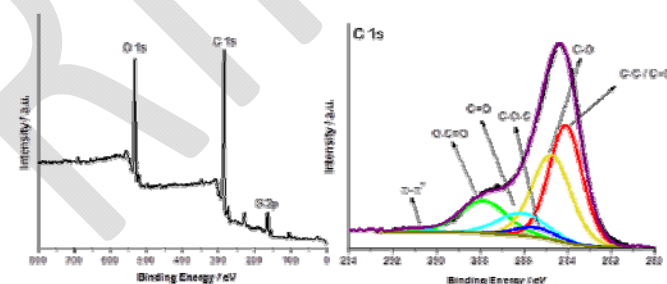


Fig. 2 XPS survey of **GQD-exTTF** and deconvoluted C 1s spectrum.

The electrochemical properties of **GQD-exTTF** were investigated by cyclic voltammetry (CV) in saturated solutions of DMSO containing 0.1M $n\text{Bu}_4\text{PF}_6$ in an argon atmosphere. The CV (Fig. S4) displays the characteristic single two-electron and chemically reversible oxidation of exTTF at +0.01 V vs. Ag/AgNO₃. Analogous results were obtained in CV analyses of an exTTF reference and CND-exTTF conjugates.¹⁰

Following the ground state characterization of **GQD-exTTF** the excited state features of **GQD-exTTF** were explored. Fluorescence spectroscopy reveals a nearly quantitative quenching of the GQD emission after their covalent functionalization with exTTF units (Fig. S6). In order to prove the existence of a charge transfer process behind this quenching, transient absorption spectroscopic measurements with **GQD-exTTF** have been carried out. Excitation at 387 nm leads to the formation of an exTTF centered excited state with an absorption minimum at 440 nm and absorption maxima at 474, 610, and 710 nm. In contrast, to the exTTF and GQD references, this transient converts into a new transient within two picoseconds. This new transient is characterized by transient maxima at 467, 546, 610, and 674 nm as well as a distinct 440 nm transient minimum, which are in sound

agreement with pulse radiolytic findings regarding the oxidation of exTTF.^{18,21-22} In other words, charge separation, in which exTTF are one-electron oxidized and GQD are one-electron reduced, evolves upon formation of the initial excited state. Finally, the charge separated state recombines to the ground state on a timescale of tens of picoseconds. To gain deeper insights into the excited state dynamics, we conducted multi wavelength analyses. In Fig. 3 the species associated spectra (SAS) and the corresponding concentration profiles are shown. The spectral features of the SASs are in accordance with the proposed kinetic model, that is, an exTTF based excited state (SAS1) with a lifetime of 2.0 ps and a GQD⁻-exTTF⁺ charge separated state (SAS2) with a lifetime of 54 ps. Notable is the lifetime of the GQD⁻-exTTF⁺ charge separated state (SAS2), which is appreciable longer than that determined in the corresponding CND conjugates.¹⁰ The less amorphous character of GQD compared to CND is likely to facilitate a better delocalization of the electrons along the carbon network.

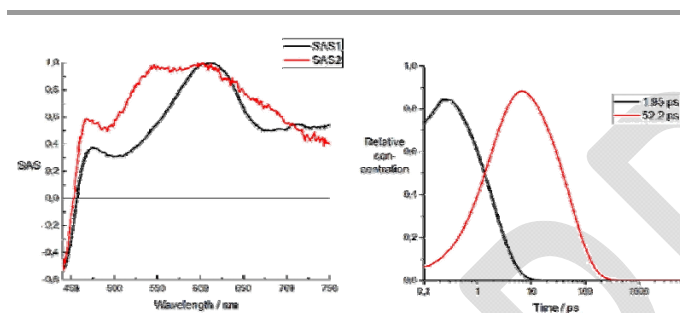


Fig. 3 Top: Normalized species associated transient absorption spectra (SAS1 and SAS2) for GQD-exTTF obtained at 22 °C in DMSO. Bottom: corresponding concentration profiles.

In conclusion, we have synthesized GQD-exTTF electron-donor acceptor nanoconjugates through the reaction of edge-oxidized GQD, obtained from graphite, with 2-hydroxymethyl-exTTF. Analyses by means of AFM, TGA, FTIR, Raman, XRD, and absorption underlined the graphitic nature of the GQD core and confirmed the covalent bonding of exTTF to GQD. When considering excited-state interactions, a prominent quenching of the yellowish emission of GQD is noticed as consequence of a charge separation, which was confirmed by transient absorption measurements. Remarkably, charge-recombination in GQD-exTTF (54 ps) is slower than in CND-exTTF (13 ps),¹⁰ a fact related with the different structure of GQD and CND. These results appear particularly promising in light of further developments in GQD-based electron-donor acceptor systems as new and promising materials for solar-energy conversion applications.

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Conflicts of interest

There are no conflicts to declare.

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Electron transfer investigations with graphene quantum dots reveal a slower charge recombination than with carbon nanodots in tetrathiafulvalene nanoconjugates

