Interfacing transition metal dichalcogenides with carbon nanodots for managing photoinduced energy and charge-transfer processes

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**ABSTRACT:** Exfoliated semiconducting MoS$_2$ and WS$_2$ were covalently functionalized with 1,2-dithiolane-modified carbon nanodots (CNDs). The newly synthesized CND-MoS$_2$ and CND-WS$_2$ hybrids were characterized by spectroscopic, thermal and electron microscopy imaging methods. Based on electronic absorption and fluorescence emission spectroscopy, modulation of the optoelectronic properties of TMDs by interfacing with CNDs was accomplished. Electrochemical studies revealed facile oxidation of MoS$_2$ over WS$_2$ in the examined hybrids, suggesting it to be better electron donor. Excited state events, investigated by femtosecond transient absorption spectroscopic studies, revealed ultrafast energy transfer from photoexcited CNDs to both MoS$_2$ and WS$_2$. Interestingly, upon MoS$_2$ photoexcitation charge transfer from an exciton dissociation path of MoS$_2$ to CNDs, within CND-MoS$_2$, was observed. However, such process in CND-WS$_2$ was found to be absent due to energetic reasons. The present study highlights the importance of TMD-derived donor-acceptor hybrids in light energy harvesting and optoelectronic applications. Furthermore, the fundamental information obtained from the current results will benefit design strategies and impact the development of additional TMD-based hybrid materials to efficiently manage and perform in electron-transfer processes.

**INTRODUCTION**

Carbon nanodots (CNDs) are recognized as promising materials for energy conversion applications.$^{1-12}$ In general, CNDs are photochemically stable,$^4$ show varied solubility in aqueous and organic media$^6$ and possess size in the order of 1-10 nm.$^6,7$ The CNDs are abundantly prepared by economic, facile and environmental benign routes, mainly involving polycondensation reactions of small organic molecules at medium or elevated temperatures under hydrothermal or microwave irradiation conditions.$^5-10$ Importantly, the surface of CNDs can be decorated with diverse functional units, which can serve as anchors to conjugate other species en route the preparation of functional hybrid nanomaterials. Notably, depending on the precursors employed for the synthesis, the periphery of the surface of CNDs can be decorated with diverse functional units, which can serve as anchors to conjugate other species en route the preparation of functional hybrid nanomaterials. For example, CNDs have been covalently conjugated with carbon nanotubes,$^{11}$ porphyrins$^{12}$ and extended tetrathiafulvalene (ex-TTF)$^{13}$ and found to participate in photoinduced charge-transfer processes. Among the marked characteristics of CNDs are the broad and tunable absorption in the visible region and the intrinsic photoluminescence,$^{14}$ while interestingly, CNDs can act as either electron donors or acceptors, owed to their bivalent redox character.$^{15}$ This is to say that upon photoirradiation, CNDs donate electrons when assembled with carbon nanotubes or perylenediimides,$^{11,16,17}$ and accept electrons upon interaction with porphyrins and exTTF.$^{12,13,18}$

Conversely, the fascination of transition metal dichalcogenides (TMDs) for energy-related applications,$^{19-22}$ attributed to their astounding optoelectronic properties and high electrical conductivity$^{23}$ has become progressively apparent. Molybdenum disulfide MoS$_2$ and tungsten disulfide WS$_2$, as the most fascinated and examined TMDs, consist of an atomic thick layer of transition metals sandwiched by two atomic layers of sulfur atoms.$^{24,25}$ Even though the crystal structure of TMDs can greatly vary, depending on the number of d-electrons of the transition metal, the most commonly observed polytypes are those with trigonal prismatic $D_{3h}$ symmetry possessing semiconducting properties and with octahedral $O_6$ coordination which show metallic behavior.$^{26}$ Delaminated TMDs can be obtained by exfoliation of the bulk counterpart and depending on the exfoliating agent employed, different polytypes are derived. For instance, treatment of bulk TMDs with organometallic media results to the metastable metallic polytype which converts to the semiconducting one by annealing, with electron-transfer phenomena governing the exfoliation process.$^{27,31}$ On the other hand, chlorosulfonic acid acting as Bronstead acid partially protonates the sulfur atoms of MoS$_2$ and WS$_2$, without oxidizing them, yielding semiconducting exfoliated nanosheets due to the development of repulsive electrostatic forces between the layers of TMDs.$^{32}$
Managing and controlling the electronic properties of semiconducting TMDs, which are governed by excitonic transitions, is mandatory for their realization as prototype devices in energy-related applications. To this end, among other sophisticated and complicated processes employed in nanosized semiconducting materials, a facile yet straightforward approach to gain precise control over the optoelectronic properties is by decorating the surface of TMDs with photo- and/or electroactive species and tuning the charge-carrier density.\(^{34}\) Hence, covalent functionalization unlocks the potentiality of TMDs by opening new opportunities and broadening the spectrum of applications.\(^{34,39}\) In a prominent example, exploiting the high binding affinity of 1,2-dithiolanes for transition metal atoms with chalcogen vacant sites, the covalent functionalization of exfoliated semiconducting TMDs was accomplished.\(^{39}\) Nevertheless, interfacing TMDs with photoactive species via robust covalent bonding toward the development of advanced hybrid materials has yet to be fully advanced. Veritably, the development of such hybrids is timely and surely deserves investigation, especially in the context of their ability to function as donor-acceptor systems upon photoillumination.

With all the above in mind, CNDs and TMDs as two highly promising nanomaterials for energy conversion, each one possessing unique characteristics and properties, were combined via robust covalent bonding en route the realization of novel donor-acceptor hybrids. Specifically, herein we report on the conjugation of modified CNDs incorporating 1,2-dithiolane moieties at the edges of exfoliated semiconducting MoS\(_2\) and WS\(_2\) and perform a comprehensive photophysical study. With the current approach, modulation and engineering of the optoelectronic properties of photoexcited TMDs was accomplished, by employing CNDs as electron acceptors, via photoinduced electron transfer processes to occur from MoS\(_2\), but not from WS\(_2\) to CNDs. The newly prepared CND-MoS\(_2\) and CND-WS\(_2\) hybrid materials were fully characterized by complementary spectroscopic, thermal and electron microscopy imaging means, undoubtfully verifying the structures derived by the functionalization process. The optical and redox properties of CND-MoS\(_2\) and CND-WS\(_2\) were probed by electronic absorption, fluorescence emission spectroscopy and electrochemistry, respectively, revealing the existence of excited state intrahybrid electronic interactions between the two species, while also showing that MoS\(_2\) was a better electron donor compared to WS\(_2\). Furthermore, with the aid of femtosecond transient spectroscopy by exciting the TMD part within the hybrid materials, strong electronic interactions between the two species leading to photoinduced charge-separation only within CND-MoS\(_2\) but not for CND-WS\(_2\) were identified. In addition, upon excitation of CNDs in CND-TMD ultrafast energy transfer from excited CNDs to both MoS\(_2\) and WS\(_2\) was identified. The fundamental information obtained from the current study will impact the development of additional TMD-based hybrid materials to efficiently manage and perform in electron-transfer processes aiming to photovoltaic and solar energy related applications.

**RESULTS AND DISCUSSION**

Initially, CNDs featuring plethora of free amine groups were prepared by polycondensation of citric acid and ethylenediamine, followed by addition of butylamine. The latter enhances the lipophilicity of CNDs, by introducing butyl units, while at the same time consumes all remaining carboxylic acid groups, stopping the growth of the nanoparticles. Next, lipoic acid activated by (3-dimethylaminopropyl)-N'-ethylcarbodiimide was condensed to yield modified CNDs bearing 1,2-dithiolanes as substituents on the periphery of their structure. Spectroscopic characterization by \('^\text{H}NMR\) and IR (Supporting Information, Figures S1, S2) verified the structure of modified CNDs and the success of synthesis. Further proof was delivered by the Kaiser test, where the amount of free amines on CNDs decreased significantly upon condensation with lipoic acid, from 1810 to 72 \(\mu\)mol/g. In parallel, bulk MoS\(_2\) and WS\(_2\) were wet exfoliated by chlorosulfonic acid,\(^{32}\) and following the functionalization methodology for TMDs with 1,2-dithiolanes,\(^{39,41}\) the conjugation of modified CNDs was accomplished, furnishing CND-MoS\(_2\) and CND-WS\(_2\) according to Scheme 1.

**Scheme 1. Illustrative preparation of CND-MoS\(_2\) and CND-WS\(_2\) upon covalent 1,2-dithiolane functionalization of exfoliated semiconducting MoS\(_2\) and WS\(_2\) nanosheets.**

The newly derived hybrid materials were found to be soluble in polar solvents such as DMF, \(\alpha\)-dichlorobenzene and methanol, while remained insoluble in less polar and apolar solvents such as dichloromethane, toluene and hexane. In fact, CND-MoS\(_2\) and CND-WS\(_2\) showed the highest solubility in DMF, with the corresponding registered values to be 0.48 and 0.44 mg/mL, respectively. Notably, the stability of CND-MoS\(_2\) and CND-WS\(_2\) in DMF was high, evidenced by the absence of precipitated material even after a period of few months.

Next, complementary characterization of CND-MoS\(_2\) and CND-WS\(_2\) by IR and Raman spectroscopy, thermogravimetric analysis (TGA) and transmission electron microscopy (TEM) imaging was performed. The presence of characteristic bands at 1640 and 1550 cm\(^{-1}\), related with stretching and bending
modes of carbonyl amide vibrations, were evident in the ATR-IR spectrum of CND-MoS$_2$ and CND-WS$_2$ (Supporting Information, Figure S3). In addition, C-H stretching vibrations at 2960 and 2915 cm$^{-1}$ due to the alkyl chain of 1,2-dithiolane were present.

Comparing Raman spectra of exfoliated MoS$_2$ and CND-MoS$_2$, obtained upon excitation under on-resonance conditions at 633 nm and normalized at the $A_{1g}$ mode at 404 cm$^{-1}$, it was found that the intensity of the 2LA(M) band associated to disorder and defects$^{42}$ and located at 447 cm$^{-1}$ was found decreased in CND-MoS$_2$ as compared to that owed to exfoliated MoS$_2$ (Figure 1a).$^{38,43}$ The latter comes as a result of the reduced number of S defects due to edge functionalization of MoS$_2$. Moreover, the absence of the characteristic phonon modes of metallic polytype MoS$_2$ so-called $J_1$, $J_2$ and $J_3$ at 150, 225 and 325 cm$^{-1}$, respectively,$^{44,45}$ ascertained the semiconducting behavior of MoS$_2$ in the CND-MoS$_2$ hybrid material. Regarding CND-WS$_2$, bands due to 2LA(M), $E_{2g}$, and $A_{1g}$, upon on-resonance excitation at 514 nm, were evident at 350, 354 and 419 cm$^{-1}$, with the intensity of the 2LA(M) mode decreased by 20% as compared to exfoliated WS$_2$ (Figure 1b). Furthermore, for both CND-MoS$_2$ and CND-WS$_2$, the $A_{1g}$ and $E_{1g}$ modes found red-shifted by 1-2 cm$^{-1}$ as compared to the values registered for exfoliated MoS$_2$ and WS$_2$ respectively. The latter is attributed to intrahybrid charge-transfer phenomena developed between the CNDs and the TMDs, in accordance with literature reports.$^{46,47}$ Since CNDs are highly fluorescent, weak and broad Raman bands attributed to – NC=O, C=O and C-H units were observed for both CND-MoS$_2$ and CND-WS$_2$ only upon excitation at 1064 nm (Supporting Information, Figure S4).

The loading of CNDs conjugated onto MoS$_2$ and WS$_2$ in CND-MoS$_2$ and CND-WS$_2$ was evaluated by TGA (Figure 1c). The modified CNDs bearing 1,2-dithiolane units were thermally stable up to 200 °C under nitrogen atmosphere, while they lost 65% of mass at the temperature range 200-500 °C. Since MoS$_2$ and WS$_2$ are thermally stable in that temperature range, the observed mass loss for CND-MoS$_2$ and CND-WS$_2$, 7.5% and 3.0% respectively, is related to the decomposition of modified CNDs present in the two hybrids. Although this is a relatively small mass loss, it is consistent with the edge functionalization of the limited S vacant sites of MoS$_2$ and WS$_2$.\[39\]

The CND-MoS$_2$ and CND-WS$_2$ hybrids were morphologically imaged by TEM. A few drops of a dispersion of the materials in hexane were deposited on the TEM grid and imaged after the solvent was evaporated. Extensive imaging of several different areas and flakes of the CND-MoS$_2$ and CND-WS$_2$ hybrid materials revealed that the size of MoS$_2$ and WS$_2$ is in the order of several hundred nanometres or even micrometre (Supporting Information, Figure S5). Although mostly oligolayered flakes were observed, most likely due to restacking of the TMDs during the drying process of the sample after depositing it on the TEM grid, the presence of some monolayered ones were also identified. In order to get better insight on CND-MoS$_2$ and CND-WS$_2$, TEM studies complemented with spatially-resolved electron energy loss spectroscopy (EELS) were performed. Figures 2a and 3a show high angle annular dark field (HAADF) scanning TEM (STEM) micrographs for CND-MoS$_2$ and CND-WS$_2$, respectively. Based on the following spectroscopic/chemical TEM analyses, the bright small objects observed in these images were assigned to CNDs covalently anchored on TMD flakes. This is confirmed by energy dispersive X-ray spectroscopy (EDS) analyses (Figures 2b and 3b, for CND-MoS$_2$ and CND-WS$_2$ respectively) and EELS (Figures 2c-e and 3c-e, for CND-MoS$_2$ and CND-WS$_2$, respectively). Figure 2c displays an ADF micrograph of CND-
MoS\textsubscript{2} and an EELS spectrum-image (SPIM) was recorded in the red marked rectangular area. Three EEL spectra were extracted in the highlighted square regions (Figure 2e(i)-(iii)). Each of these three EEL spectra corresponds to the sum of 9 spectra (3x3 probe positions of the SPIM). The S-L\textsubscript{2,3} and Mo-M edges are visible in the three spectra and correspond to MoS\textsubscript{2} \textsuperscript{48,49}. It is worth mentioning that no MoO\textsubscript{x} was observed highlighting the high quality and purity of the materials. In addition, C was detected in specific areas, see the presence of the C-K edge (Figure 2e(ii)-(iii)). This C-K edge, which is superposed to the Mo-M\textsubscript{4,5} edge, is associated with the presence of CNDs within the CND-MoS\textsubscript{2} hybrid. The chemical C map obtained from the analysis of C-K edge (Figure 2d) clearly supports this finding. \textsuperscript{48,49} Indeed, CNDs are observed not only in the ADF-STEM micrograph (Figure 2c) but also in this C-map (Figure 2d). Similar assays were performed for CND-WS\textsubscript{2} and from TEM analyses (Figure 3a-e) the presence of CNDs attached on WS\textsubscript{2} was confirmed.

### Figure 2.
Representative HRSTEM-ADF images for (a, d) CND-MoS\textsubscript{2}, (b) EDS acquired on the squared white area in (a). In the red regions of (c) spectra-images SR-EELS were recorded. (d) Carbon elemental map extracted from the integrated intensity of the C-K edge of the EELS spectrum-image recorded in the red area in (c). (e) Three spectra from the sum of 9 (3x3) EELS extracted from the marked areas of the EELS SPIM of (c). The C-K edge (~284 eV) is observed in (ii) and (iii) superposed with the Mo-M edge. The S-L\textsubscript{2,3} and Mo-M edge of MoS\textsubscript{2} are visible in the three spectra ((i)-(iii)).

### Figure 3.
Representative HRSTEM-ADF images for (a, d) CND-WS\textsubscript{2}, (b) EDS acquired on the squared white area in (a). In the red regions of (c) spectra-images SR-EELS were recorded. (d) Carbon elemental map extracted from the integrated intensity of the C-K edge of the two EELS spectra-image recorded in the red area in (c). (e) Three spectra from the sum of 16 (4x4) EELS extracted from the EELS SPIM of (c), showing the S-L\textsubscript{2,3} and C-K (in this case only in (ii) and (iii)) edges. The C-K edge (~284 eV) is observed in (ii) and (iii). The S-L\textsubscript{2,3} edge is visible in the three spectra ((i)-(iii)).
and CND-WS₂ resulted in a biexponential decay, with the identification of major faster components with 1.2 and 1.1 ns lifetime, corresponding to the quenching of singlet excited state of CNDs in CND-MoS₂ and CND-WS₂, respectively.

The electrochemical behavior of CND-MoS₂ and CND-WS₂ was successively investigated in DMF (Supporting Information, Figure S7). The cyclic voltammogram (CV) of exfoliated MoS₂ revealed irreversible oxidations at $E_{pa} = -0.08$ and 0.48 V and reductions at $E_{pc} = -1.20$ and -1.69 V vs Fe/Fe⁺. In CND-MoS₂, the first oxidation wave was too broad to pick the peak potential, while the second one was better defined with an $E_{pa} = 0.54$ V. The two reductions were located at $E_{pc} = -1.48$ and -2.20 V as a consequence of the covalent functionalization. The CV of exfoliated WS₂ revealed irreversible oxidations at $E_{pa} = 0.23$ and 0.44 V and reductions at $E_{pc} = -1.40$ and -1.98 V. Upon covalent attachment of CNDs, the oxidation waves broadened, making it difficult to identify the peak potential, while the reduction was anodically shifted to $E_{pc} = -1.37$ and -1.63 V. Importantly, both MoS₂ and WS₂ were found to be electroactive and such property persisted upon chemical functionalization with CNDs. The facile oxidation of MoS₂ over WS₂ suggests it to be better electron donor. The CV of CNDs revealed no measurable electrochemical activity within the potential window. Although shifts in the potentials were observed upon chemical functionalization of TMDs, due to irreversible nature of the redox processes, it was difficult to derive meaningful structure-redox property relations. Nonetheless, the facile oxidation of MoS₂ over WS₂ suggests it to be better electron donor. Differential spectral changes observed during the first oxidation and reduction of MoS₂ and WS₂ are shown at the Supporting Information, Figure S8. In both TMDs, reduction in peak intensity of the neutral species was observed, more so for MoS₂ compared to WS₂. Some positive spectral features in the 300-450 nm range were observed for MoS₂ during oxidation.

The excited state events were probed by femtosecond pump-probe transient absorption spectroscopy in DMF, where dispersion of the hybrids was appreciable. The samples were excited at 370 nm corresponding mainly to CNDs excitation and at 425 nm corresponding mainly to TMDs excitation. In agreement with literature reports, immediately after 425 nm excitation of exfoliated MoS₂, three minima at 503, 637 and 696 nm due to excitonic transitions as seen in the absorption spectrum, and two maxima at 595 and 663 nm corresponding to induced absorption of B and A excitons, were observed (Supporting Information, Figure S9a). During the first 10 ps, all peaks experienced blue shift ascribed to cooling of hot excitons and/or interexcitonic interactions. In the case of exfoliated WS₂, two minima at 545, and 652 nm (B and A excitons, by comparison with the absorption spectrum) and two maxima at 516 and 617 nm were observed (Supporting Information, Figure S9b). The peak positions also experienced a small blue-shift of 2 nm within the first 10 ps.

Figure 4 shows the transient absorption spectra and intensity-wavelength maps of CND-MoS₂ and CND-WS₂ dispersions in DMF at $\lambda_{exc}$ 370 nm mainly exciting the CNDs. The transient spectra of CNDs ($\lambda_{exc}$ 370 nm) revealed positive peaks at 460 and 590 nm (Supporting Information, Figure S10a) originating from transitions involving excited CNDs. The decay of these peaks was rather slow consistent with the longer fluorescence lifetime of CNDs (6.3 ns). When exfoliated MoS₂
and and WS$_2$ were excited at 370 nm (Supporting Information, Figure S10b, c), the spectra revealed features corresponding to these materials, however, with much diminished peak intensities compared to that shown in the Supporting Information, Figure S10 at $\lambda_{\text{exc}}$ 425 nm. These observations suggest that at $\lambda_{\text{exc}}$ 370 nm, in addition to CNDs, both MoS$_2$ and WS$_2$ also get excited to some extent. Interestingly, when CND-MoS$_2$ and CND-WS$_2$ were excited at 370 nm, the peaks corresponding to the excited CNDs revealed rapid deactivation with simultaneous development of strong excitonic peaks of MoS$_2$ and WS$_2$, more so for CND-MoS$_2$ than that for CND-WS$_2$ (Figure 5). These results indicate occurrence of energy transfer from singlet excited CNDs to MoS$_2$ and WS$_2$ in the hybrids. In both hybrids the excitation transfer was complete within 4-5 ps, indicating an efficient process.

Next, the hybrids were excited at 425 nm, where majority of MoS$_2$ and WS$_2$ have absorbance. The transient spectral features of CND-MoS$_2$ (Figure 6a) were distinctly different from that of exfoliated MoS$_2$ (Supporting Information, Figure S9a), especially with respect to the peak time profiles (see intensity-wavelength maps). Figure 6a(iii) shows the time profile of the 688 nm peak of exfoliated MoS$_2$ and CND-MoS$_2$ corresponding to the excitonic peak at 688 nm. The recovery of the exciton peak was slow for CND-MoS$_2$ suggesting occurrence of excited state events from the excited MoS$_2$ to the covalently linked CNDs. Earlier, a facile oxidation was observed for MoS$_2$ ($E_{pu} = -0.08$ V) suggesting that it could act as an electron donor generating charge separated state.$^{53,60}$ In such an event, charge transfer from a dissociated excitonic state would be promoted to CNDs conduction band, generating a charge separated state. The hole in MoS$_2$ layer would recover slowly due to a charge recombination process.

**Figure 5.** Femtosecond transient absorption spectra of (a) CND-MoS$_2$ and (b) CND-WS$_2$ in DMF ($\lambda_{\text{exc}}$ 370 nm). The right-hand panel shows intensity-wavelength maps.

Further, the transient data of exfoliated MoS$_2$ and CND-MoS$_2$ were subjected to global analysis for kinetic evaluations (Figure 7). Decay associated spectra of exfoliated MoS$_2$ revealed three major components; the spectrum at 2.3 ps consists of positive peaks at the spectral range, where excitonic peaks are expected. The spectrum at 1.1 ns had decay of positive transients. The final component with over 3 ns related to only the excitonic signals with positive shift relative to A exciton. Earlier, for the ultimate decay of the excitons, a lifetime of $\lambda_{\text{exc}}$ 550 nm range, ascribed to trionic state that revealed faster decay. The long-lived decay component had only the excitonic features similar to that observed for unmodified MoS$_2$. These results suggest that the charge separation occurs with a time constant of about 250 ps in the CND-MoS$_2$ hybrid.

**Figure 6.** Femtosecond transient absorption spectra of (a) CND-MoS$_2$ and (b) CND-WS$_2$ in DMF ($\lambda_{\text{exc}}$ 425 nm). The right-hand panels show (ii) intensity-wavelength map and (iii) an overlap time profile of the 688 nm of CND-MoS$_2$ (blue) and exfoliated MoS$_2$ (red) and 652 nm of CND-WS$_2$ (blue) and exfoliated WS$_2$ (red).

**Figure 7.** Decay associated spectra of (a) exfoliated MoS$_2$ and (b) CND-MoS$_2$ for the transient data shown in Figure S8a and Figure 6a.
Transient spectra recorded for CND-WS₁₂ (Figure 6b) were close to that of unmodified WS₁₂ (Supporting Information, Figure S9b). The time profiles of the 652 nm peak (Figure 6b(iii)) were superimposable suggesting lack of major excited state events such as charge transfer from excited WS₁₂ to CNDs. This could be rationalized to the harder oxidation of WS₁₂ ($E_{pa} = 0.23$) that would dampen any charge transfer events due to energy considerations. Hence, no further analysis was performed on this hybrid material.

**CONCLUSIONS**

In summary, following the 1,2-dithiolane functionalization protocol for TMDs, the covalent grafting of CNDs onto exfoliated MoS₂ and WS₂ was accomplished. The newly prepared CND-MoS₂ and CND-WS₂ hybrid materials were fully characterized by complementary spectroscopic, thermal and electron microscopy imaging techniques. Furthermore, electrochemical assays revealed that MoS₂ was a better electron donor compared to WS₂. Photochemical events upon preferential photoexcitation of CNDs and TMDs were probed. Excitation of CND-MoS₂ and CND-WS₂ at 370 nm revealed ultrafast energy transfer from excited CNDs to MoS₂ and WS₂, while exciting the TMDs within the hybrid materials at 425 nm, charge transfer in CND-MoS₂ but not in CND-WS₂ was seen. The observed excited state electron transfer processes bring us one-step closer to utilizing the covalently modified TMDs in donor-acceptor type hybrids for energy harvesting applications.

**EXPERIMENTAL SECTION**

**Electron microscopy imaging.** STEM imaging and EELS studies were conducted using an aberration-corrected FEI Titan Low-Base microscope operated at 80 kV. This microscope was equipped with a Cs probe corrector and a Gatan Tridiem ESR 865 electron energy loss spectroscopy (EELS) spectrometer. The energy resolution was ~1 eV. The convergence and collection angles were 25 and 50 mrad, respectively. The EELS studies were conducted in STEM mode, using the spectrum-line scan mode. To increase the signal/noise ratio of the EEL spectra, the datasets were then de-noised with the open-source program Hyperspy using principal component analysis routines.

**Femtosecond transient absorption spectroscopy.** Experiments were performed using an Ultrafast Femtosecond Laser Source (Libra series) by Coherent Inc. (Santa Clara, CA) incorporating diode-pumped, mode locked Ti:Sapphire laser (Vitesse) and diode-pumped intra cavity doubled Nd:YLF laser (Evolution) to generate a compact laser output of 1.45 W. For optical detection, a Helios transient absorption spectrometer from Ultrafast Systems (Sarasota, FL) was used. The source for the pump and probe pulses were derived from the fundamental output of Libra (Compressed output 1.45 W, pulse width 100 fs) at a repetition rate of 1 kHz. About 95% of the fundamental output of the laser was introduced into a TOPAS-Prime-OPA system with 290-2600 nm tuning range from Altos Photonics Inc., (Bozeman, MT), while the rest of the output was used for generation of white light continuum. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at room temperature.

**Modified CNDs with lipoic acid.** Initially, 2g of citric acid (1 equiv.) were dissolved in DMF (10 mL) and the solution was cooled in ice bath. Then, 4.4 mL of N,N'-disopropylcarbodiimide (DIC) as coupling agent (3 equiv.) were added slowly to the solution while stirring, forming a white dispersion. After one minute, 1.9 mL of ethylenediamine (EDA) in cold water (10 mL) were poured into the reaction mixture. When the color turned yellow and then orange the fluorescent particles were formed, thus butylamine (5 mL) was added and the reaction mixture was left under stirring for 24 hours. The addition of butylamine allowed the in-situ introduction of butyl groups on the CNDs surface, enhancing lipophilicity and at the same time consuming all remaining carboxylic groups, thus stopping the growth of the nanoparticles. Then, the solution was filtered to remove the DIC urea by-product, the filtrate was washed three times with diethylether and the excess of butylamine was removed under vacuum evaporation. Finally, the water phase was purified by dialysis in ultrapure water (molecular weight cut-off = 0.5-1 kDa, 3 days). The dry product of CNDs-NH₂ (0.7 g) was obtained as a yellow powder by freeze-drying.

In the next step, CNDs-NH₂ (200 mg) were dissolved in a mixture of methanol (5 mL) and dichloromethane (25 mL) and cooled to 0 °C. In another flask, lipoic acid (300 mg) was dissolved in dichloromethane (5 mL), cooled at 0 °C and 336 mg of (3-dimethylaminopropyl)-N'-ethylcarbodiimide (EDC) were added. After 20 minutes, the lipoic acid solution was poured into that of CNDs-NH₂. The reaction mixture was left under stirring for 24 hours and after that period additional lipoic acid (100 mg) and EDC (56 mg) were added. After 3 hours the reaction mixture was extracted with distilled water, aqueous NaOH (pH=11) and with brine. The organic phase was dried over MgSO₄, the dichloromethane was partially evaporated by vacuum and diluted with ethyl acetate, resulting on the precipitation of the particles (centrifugation at 3200 rpm, 5 minutes). The redispersion-centrifugation process was repeated until the lipoic acid spot in TLC disappeared. The precipitate was dissolved again in methanol/dichloromethane 1:1 v/v and dried over MgSO₄ to obtain CNDs carrying 1,2-dithiolane chains as a brown solid, after vacuum evaporation of the solvent.

**Exfoliation of semiconducting TMDs.** Bulk TMDs (150-200 mg) were dispersed in chlorosulfonic acid and sonicated for 2 hours at room temperature. The solution was left under stirring during a month, occasionally sonicated for 30 seconds. Afterwards it was added cold water to the solution under stirring, drop by drop and extremely carefully. Please notice that the reaction is exothermic and releases gaseous HCl. Next, the mixture was filtrated on a PTFE filter of 0.2 µm pore, 50 mL) in another flask, exfoliated TMDs (20 mg) were dispersed in DMF (10 mL) by sonication (10 min) and dropped in the CNDs solu-
tion. The flask was covered with aluminum foil and the reaction mixture was stirred at 70 °C for 4 days. After that period, it was cooled and filtered through a PTFE membrane (0.2 nm pore size). The solid residue was extensively washed with methanol and dichloromethane to obtain the CND-TMDs.

ASSOCIATED CONTENT
Supporting Information
General instrumentation, \(^1\)H NMR, ATR-IR, Raman, UV-Vis and femtosecond transient absorption spectra and cyclic voltamograms. The Supporting Information is available free of charge on the ACS Publications website.

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ACKNOWLEDGMENT
This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 642742. Support of this work by the project “Advanced Materials and Devices” (MIS 5002409) which is implemented under the “Action for the Strategic Development on the Research and Technological Sector”, funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" co-financed by Greece (Ministry of Economy and Development, NSRF 2014-2020) and EU (European Regional Development Fund) to N. T. and the US-NSF (grant 1401188 to F. D.) is acknowledged. The HR-STEM and STEM-EELS studies were conducted at the Laboratorio de Microscopias Avanzadas, Universidad de Zaragoza, Spain. R. A. acknowledges support from Spanish MINECO grant MAT2016-79776-P (AEI/FEDER, UE) and from EU H2020 “Graphene Flagship” grant agreement 785219. W. K. M. and A. M. B. acknowledge Spanish MINECO grant ENE2016-79282-C5-1-R (AEI/FEDER, EU) and the Government of Aragon through project DGA-T03_17R (FEDER, EU).

ABBREVIATIONS
CNDs, carbon nanodots; exTTF, extended tetrafluoravulene; TMDs, transition metal dichalcogenides; TGA, thermogravimetric analysis; TEM, transmission electron microscopy; EELS, electron energy loss spectroscopy; HAADF, high angle annular dark field; STEM, scanning transmission electron microscopy; EDS, energy dispersive X-ray spectroscopy.

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