

Supporting Information

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

Lorenzo Vallan,^{‡#} Ruben Canton-Vitoria,^{§#} Habtom B. Gobeze,^{¶#} Youngwoo Jang,[¶] Raul Arenal,^{*,¥} Ana M. Benito,[‡] Wolfgang K. Maser,^{*,‡} Francis D' Souza,^{*,¶} Nikos Tagmatarchis^{*,§}

[§] Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, 11635 Athens, Greece.

E-mail: tagmatar@eie.gr

[‡] Instituto de Carboquímica, (ICB-CSIC), C/Miguel Luesma Castán 4, E-50018 Zaragoza, Spain.

[¶] Department of Chemistry, University of North Texas, 1155 Union Circle, 305070 Denton, TX 76203-5017, USA.

[§] Laboratorio de Microscopias Avanzadas, Instituto de Nanociencia de Aragon. Universidad de Zaragoza, 50018 Zaragoza, Spain.

[¥] ARAID Foundation, 50018 Zaragoza, Spain.

[#] These authors contributed equally.

Experimental Section

Steady-state UV-Vis electronic absorption spectra were recorded on a PerkinElmer (Lambda 19) UV-Vis-NIR spectrophotometer. Steady-state emission spectra were recorded on a Fluorolog-3 JobinYvon-Spex spectrofluorometer (model GL3-21). Pico-second time-resolved fluorescence spectra were measured by the time-correlated-single-photon-counting (TCSPC) method on a Nano-Log spectrofluorometer (Horiba JobinYvon), by using a laser diode as an excitation source (NanoLED, 375 nm) and a UV-Vis detector TBX-PMT series (250-850 nm) by Horiba JobinYvon. Lifetimes were evaluated with the DAS6 Fluorescence-Decay Analysis Software. Mid-infrared spectra in the region 500-4500 cm^{-1} were obtained on a Fourier transform IR spectrometer (Equinox 55 from Bruker Optics) equipped with a single reflection diamond ATR accessory (DuraSamp1IR II by SensIR Technologies). A drop of the solution was placed on the diamond surface, followed by evaporation of the solvent, in a stream of nitrogen, before recording the spectrum. Typically, 100 scans were acquired at 2 cm^{-1} resolution. Micro-Raman scattering measurements were performed at room temperature in the backscattering geometry using a RENISHAW inVia Raman microscope equipped with a CCD camera and a Leica microscope. A 2400 lines mm^{-1} grating was used for all measurements, providing a spectral resolution of $\pm 1 \text{ cm}^{-1}$. As an excitation source the Ar^+ laser (633 nm with less than 0.265 mW laser power or 514 nm with less than 0.45 mW laser power). Measurements were taken with 15 seconds of exposure times at varying numbers of accumulations. The laser spot was focused on the sample surface using a long working distance 50x objective. Raman spectra were collected on numerous spots on the sample and recorded with Peltier cooled CCD camera. The data were collected and analyzed with Renishaw Wire and Origin software. FT-Raman spectra were acquired on a Bruker RFS100 with less than 300 mW laser power. Thermogravimetric analysis was performed using a TGA Q500 V20.2 Build 27 instrument by TA in a nitrogen (purity >99.999%) inert atmosphere. The microwave-assisted reaction was performed in a CEM Discover SP reactor employed in open-batch modality. Particle height distribution analysis was carried out by using the Nanoscope Analysis Version 1.5 software (Veeco Ins). Elemental analyses were performed in a Thermo Flash EA 1112 instrument with $\sim 3 \text{ mg}$ of powder samples. The DLS measurements were recorded on a Malvern Nano Zetasizer HT, on a 10 mm path-length plastic cuvette. ^1H and ^{13}C NMR spectra were recorded at 25 $^\circ\text{C}$ on a Bruker AV500 spectrometer.

Cyclic and differential pulse voltammograms were recorded on an AMETEK PARSTAT 4000A Potentiostat/Galvanostat/EIS Analyzer using a three-electrode system. A platinum button electrode was used as the working electrode. A platinum wire served as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. Ferrocene/ferrocenium redox couple was used as an internal standard. All the solutions were purged prior to electrochemical and spectral measurements using argon gas.

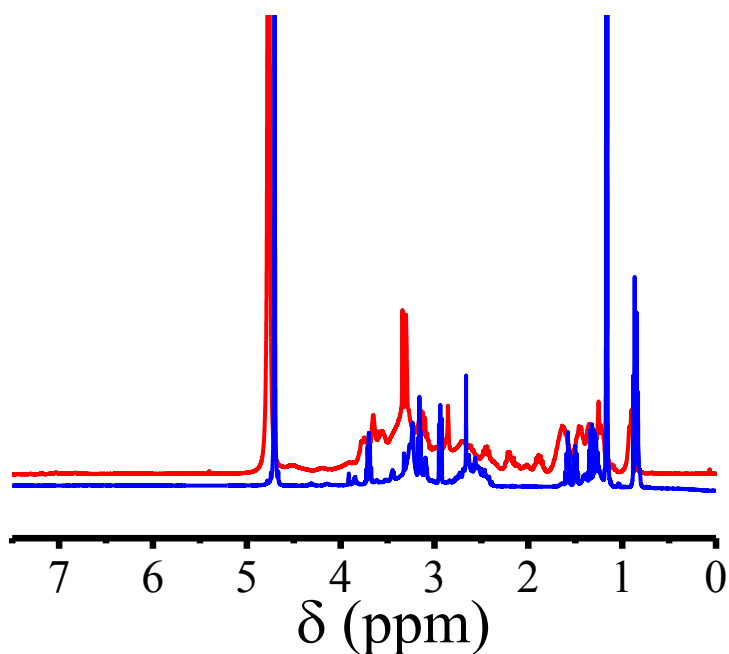


Figure S1. ^1H NMR spectrum for as-produced CNDs (blue) and 1,2-dithiolane modified CNDs (red). All the signals for the as-produced CNDs are found in the aliphatic region and correspond to the methylene protons of citric acid and ethylenediamine structural components (4.0-2.3 ppm) and butyl units (1.6-0.7 ppm). In the 1,2-dithiolane modified CNDs, multiplets appear between 2.6 and 1.5 ppm, corresponding to the protons of the lipoic amide moiety condensed onto the periphery of CNDs.

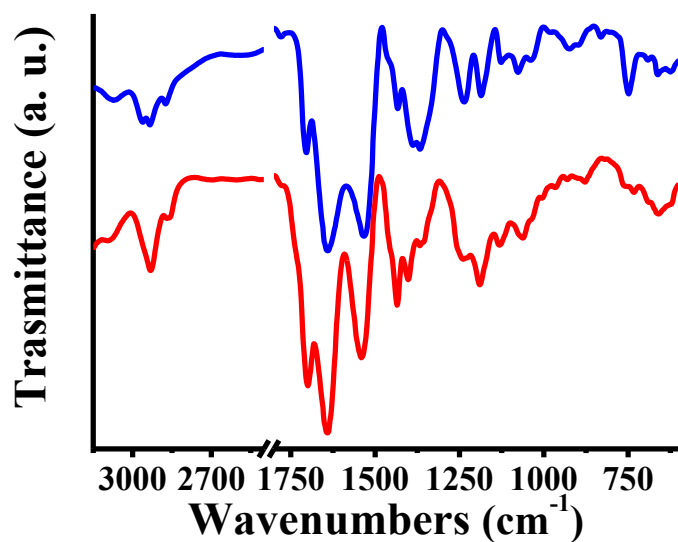


Figure S2. ATR-IR spectra of as-produced CNDs (blue) and 1,2-dithiolane modified CNDs (red). The IR features on the as-produced CNDs are assigned as to O-H and N-H stretching vibrations at 3300-3000 cm^{-1} , C-H stretching at 2920 cm^{-1} , C=O stretching of free carboxylic acid units at 1705 cm^{-1} , C=O stretching of amide units at 1640 and 1630 cm^{-1} , and C-O and C-N stretching at 1440-1360 cm^{-1} . In the modified CNDs, the intensity for the C=O stretching amide band was increased.

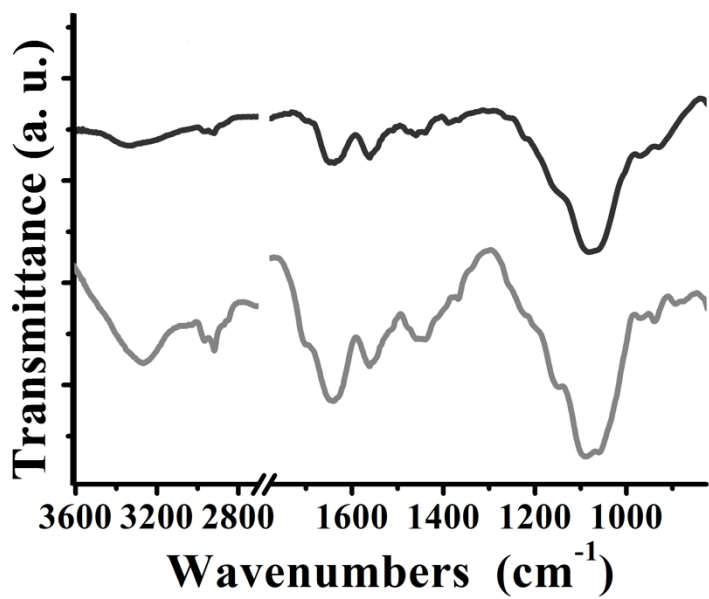


Figure S3. (a) ATR-IR spectra of CND-MoS₂ (black) and CND-WS₂ (grey).

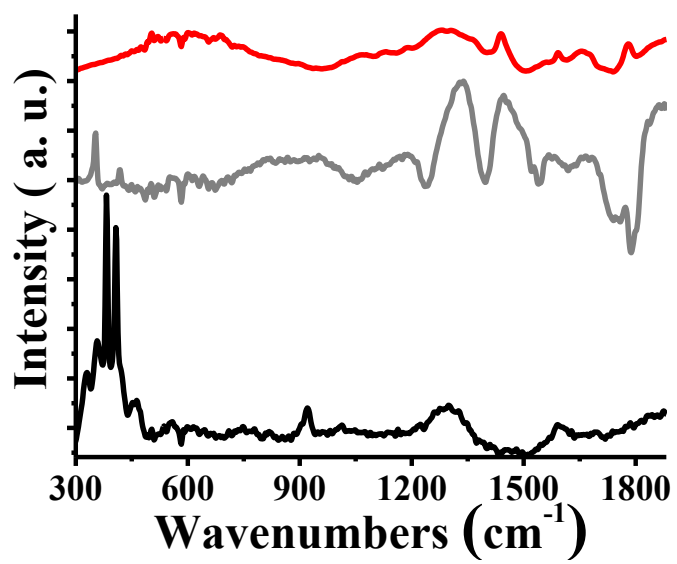


Figure S4. Raman spectra (1064 nm) for CNDs (red), CND-MoS₂ (black) and CND-WS₂ (grey).

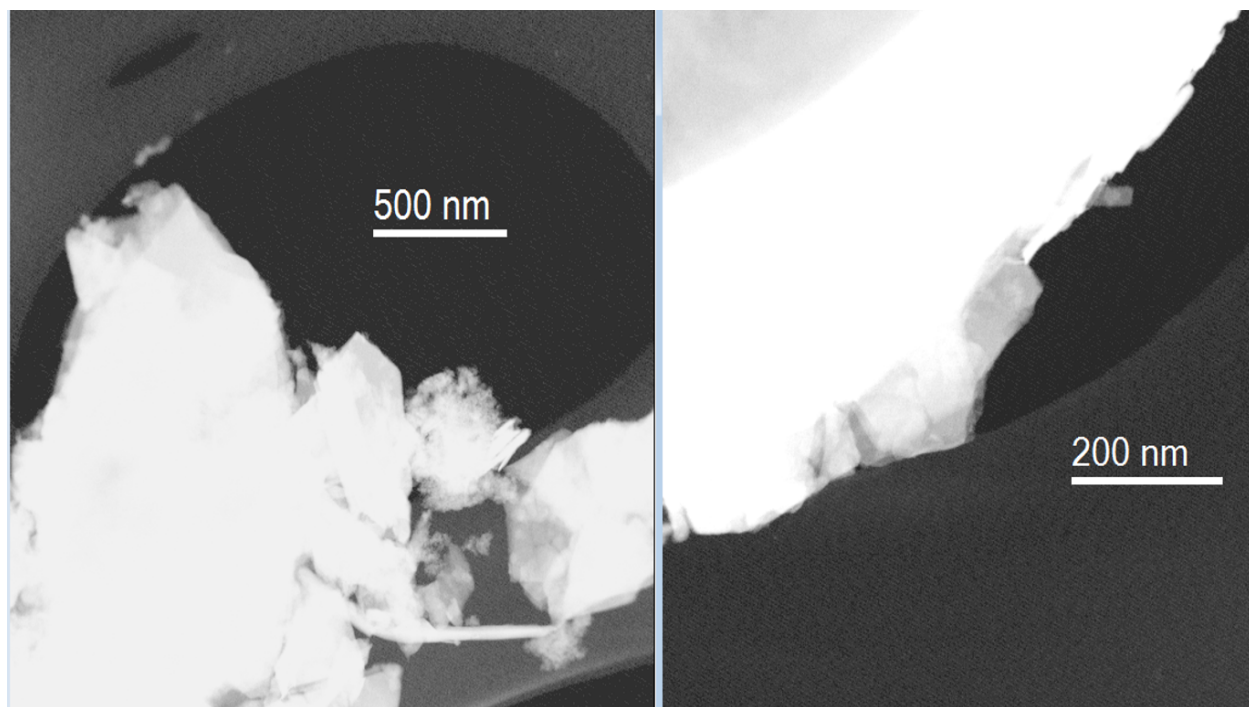


Figure S5. Representative low-magnification HR-STEM-ADF images for CND-MoS₂ (left) and CND-WS₂ (right).

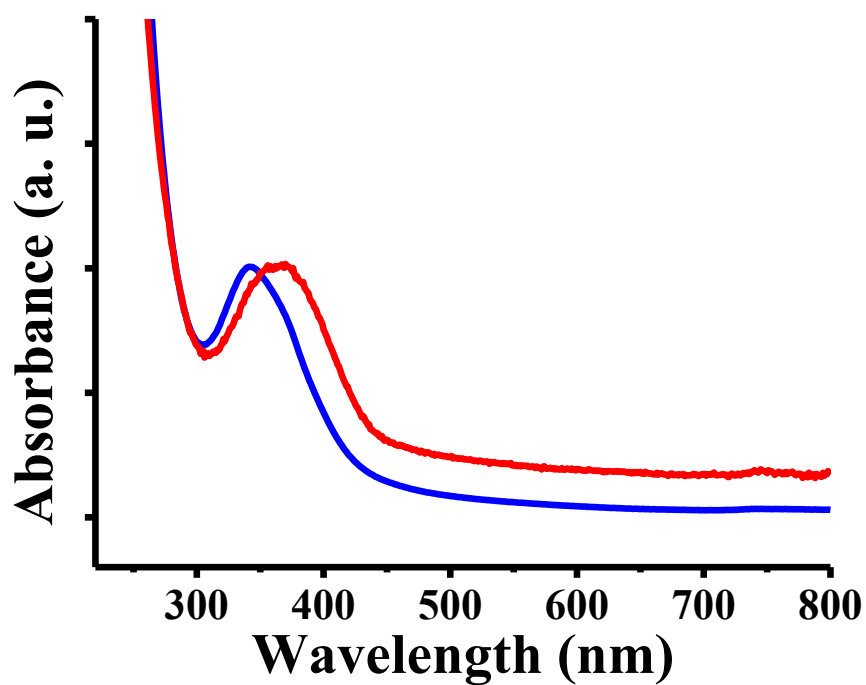


Figure S6. UV-Vis spectra of as-produced CNDs (blue) and 1,2-dithiolane modified CNDs (red), obtained in methanol. The characteristic absorbance of CNDs is red-shifted from 345 nm for the as-produced CNDs to 370 nm for the 1,2-dithiolane modified CNDs.

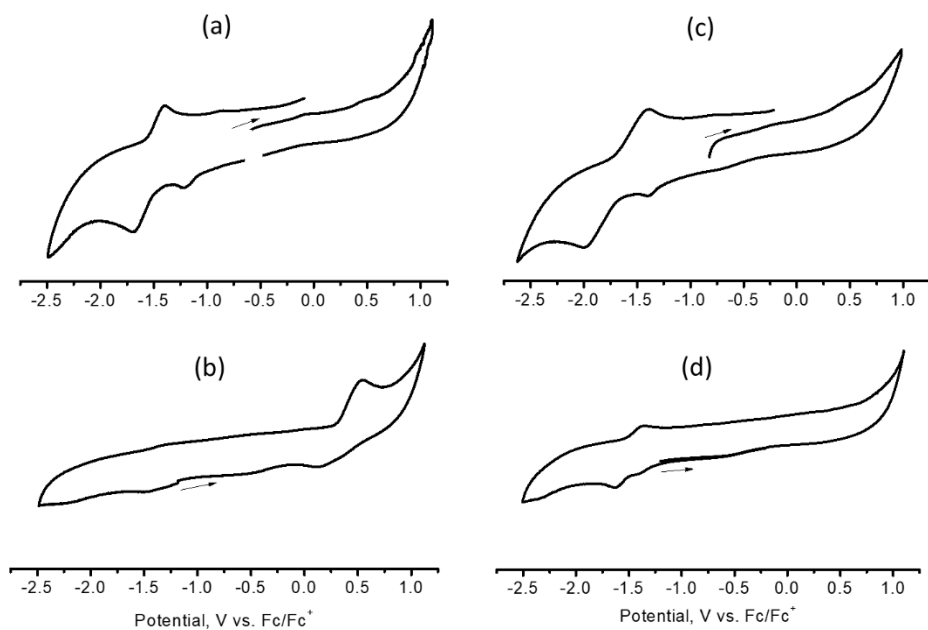


Figure S7. Cyclic voltammograms of (a) exfoliated MoS₂, (b) exfoliated WS₂, (c) CND-MoS₂, and (d) CND-WS₂ in DMF containing 0.1 M of n-Bu₄NClO₄ as electrolyte. Scan rate = 100 mV/s.

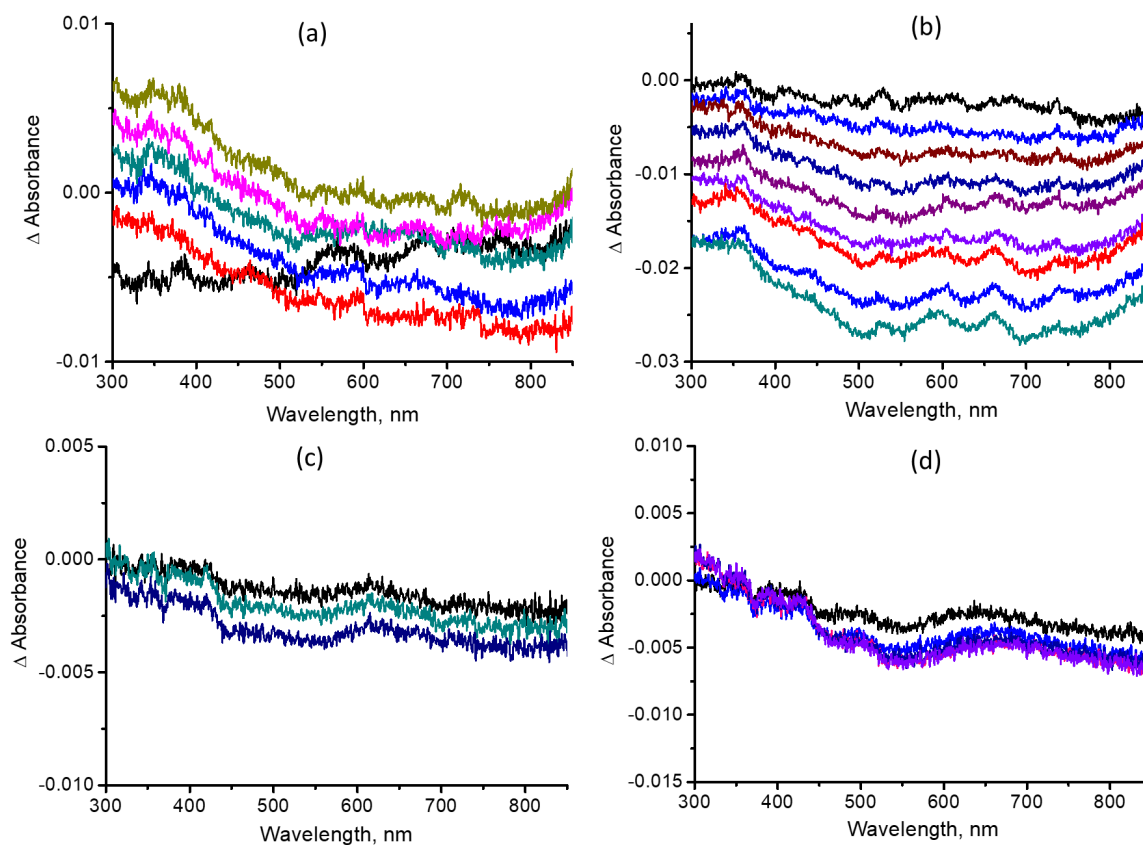


Figure S8. Spectral changes observed during (a) first oxidation and (b) first reduction of exfoliated MoS₂, and (c) first oxidation and (d) first reduction of exfoliated WS₂ in DMF containing 0.2 M *n*-BuN₄ClO₄ as electrolyte.

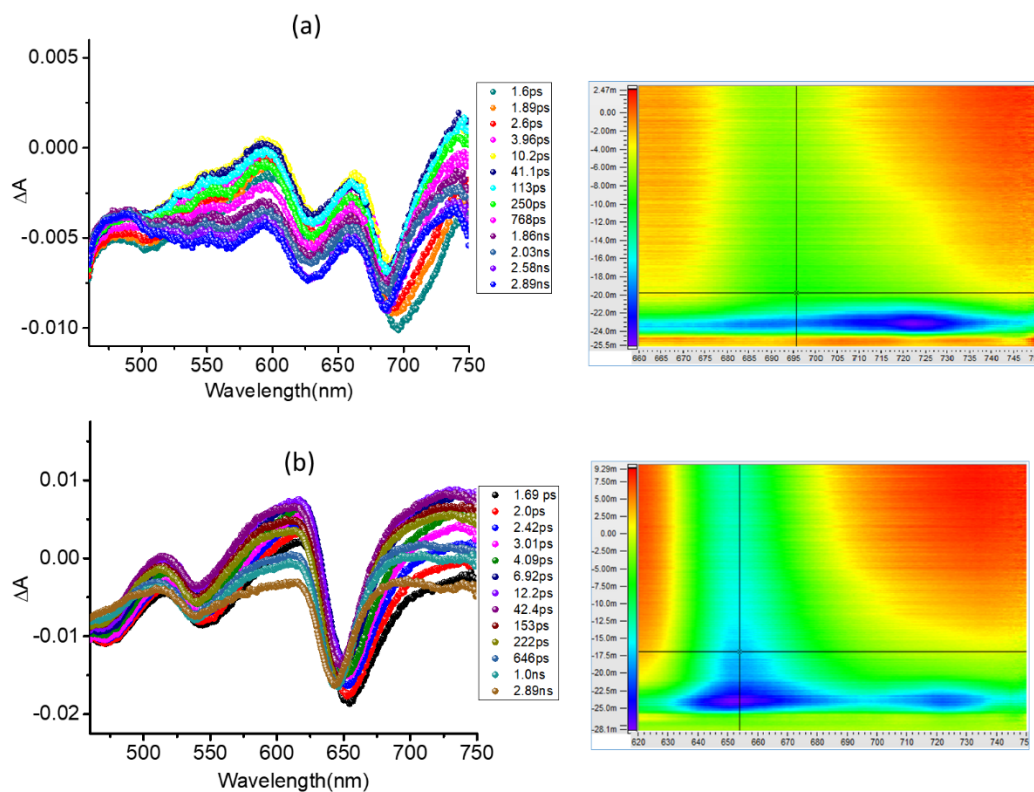


Figure S9. Femtosecond transient absorption spectra at the indicated delay times of exfoliated (a) MoS₂ and (b) WS₂, in DMF at the excitation wavelength of 425 nm. The right-hand panel shows intensity-wavelength maps.

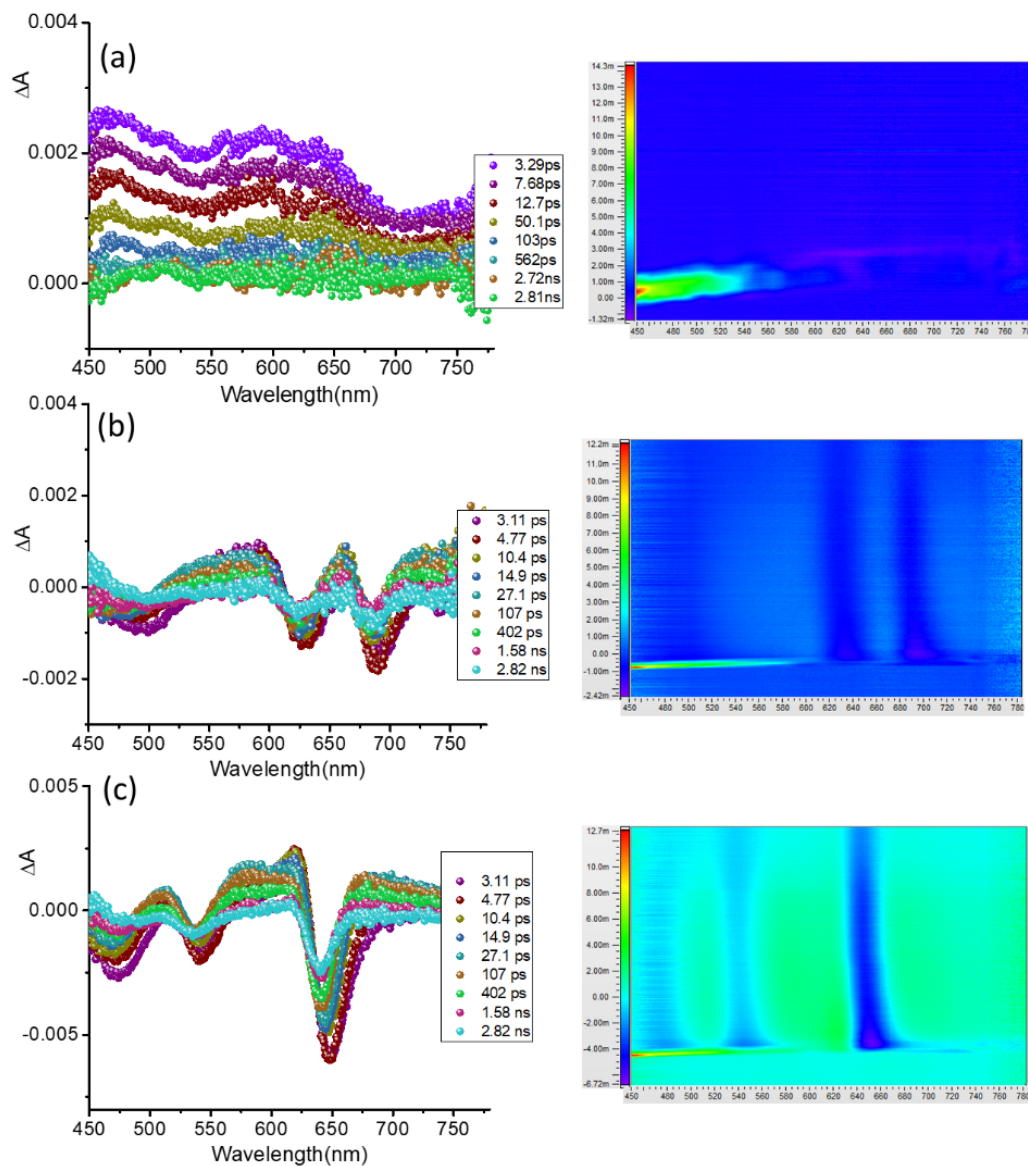


Figure S10. Femtosecond transient absorption spectra at the indicated delay times of (a) CNDs, (b) MoS₂ and (c) WS₂ dispersions in DMF at the excitation wavelength of 370 nm. The right-hand panel shows intensity-wavelength maps.