# ELECTRONIC SUPPMENTARY INFORMATION

## One-step covalent hydrophobic/hydrophilic functionalization of chemically exfoliated molybdenum disulfide nanosheets with RAFT derived polymers

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## Instrumentation

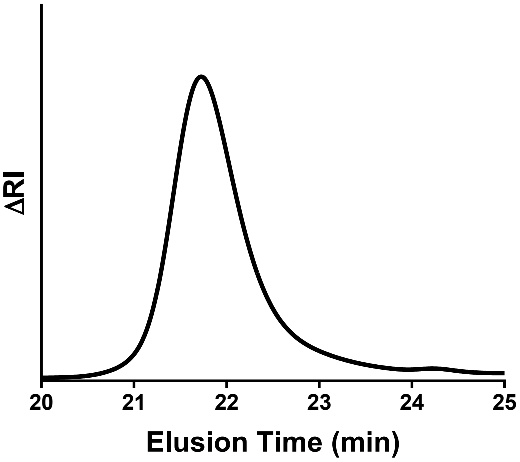
Ultrasonication was performed with the aid of a Bandelin Sonoplus GM3200 equipped with a VS 70 T extended probe at 50% power (75W, 20kHz). $^1$H NMR spectra was recorded using a Varian 300 MHz spectrometer. UV-Vis spectra recorded on a Perkin-Elmer Lambda 19 UV-Vis-NIR spectrophotometer and the absorption of water was subtracted. FT IR spectra were recorded on Bruker Equinox 55 FTIR spectrometer equipped with a Pike Miracle Ge ATR accessory. 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 grating (for 514 nm) and 2400 lines/mm grating (for 633 nm) were used, providing a spectral resolution of ± 1 cm$^{-1}$. As an excitation source the Ar (514 nm) and He/Ne laser (633 nm) were used. Measurements were taken with 10s seconds of exposure times and laser power ~0.3 mW/cm$^2$ to prevent overheating and damage of the basal plane. The laser spot was focused on the sample surface using a long working distance 50x (L50) objective. Raman spectra were collected on numerous spots on the sample and recorded with a Peltier cooled CCD camera. The data were collected and analyzed with Renishaw Wire and Origin software. Fluorescence spectra were recorded in aqueous (distilled water) solutions on a Fluorolog-3 JobinYvon-Spex spectrofluorometer (model GL3-21) equipped with a UV-Vis detector (200-800nm) operated at room temperature. High-resolution transmission electron microscopy (HRTEM) imaging has been performed in a FEI Titan Cube microscope (equipped with a spherical aberration corrector) operating at 80 kV.

## Preparation of chemically exfoliated $MoS_2$ nanosheets (*ce*-$MoS_2$)

[Extreme care must be taken when working with *n*-BuLi, since it reacts violently with humidity and water and is pyrophoric. A well-ventilated hood is also required.] Initially, 750 mg (4.68 mmol) of bulk 2H-$MoS_2$ were placed in a furnace at 300 °C for 24h. Then, the dried powder was placed in a 10 mL flask with a magnetic stir bar and cooled to room temperature under nitrogen atmosphere. Under nitrogen atmosphere, 7.5 mL (18.75 mmol) of 2.5 M *n*-BuLi were introduced and the mixture stirred vigorously for 48 h under nitrogen. After this period, the black suspension was let to settle, the intercalated solid $Li_x$-$MoS_2$ was precipitated and the supernatant *n*-BuLi solution was pipetted-off under nitrogen. Then 15 mL of dry hexane were introduced under nitrogen atmosphere and the mixture was vigorously stirred for 10 minutes. Then, the black suspension was let to settle, the intercalated solid $Li_x$-$MoS_2$ was precipitated and the supernatant containing the excess *n*-BuLi was pipetted-off under nitrogen. This step was repeated two more times to ensure the removal of excess *n*-BuLi from the reaction mixture. The residual black slurry of $Li_x$-$MoS_2$ was opened in the air and rapidly immersed in a 1L flask filled with 750 mL of cold distilled water. Water reacts rapidly with the $Li_x$-$MoS_2$ evolving gas. The immersed flask and the stir bar were removed and the mixture (C= 1 mg/mL) was ultra-sonicated for 3 h (pulse ON:3s - OFF:3s) keeping the temperature below 30 °C with the aid of an ice bath. Finally, the suspension was let to settle overnight, the top 2/3 were collected and stored in a sealed flask in the dark and below 30 °C. The concentration of the *ce*-$MoS_2$ suspension was calculated as follows: 3 mL of the suspension were filtered over a pre-weight PTFE membrane filter under vacuum and washed with distilled water and ethanol, the filter cake was dried under vacuum and weighted. Accordingly, the concentration of the suspension was calculated as high as 1 mg/mL. The suspension remains stable without any precipitation for several weeks. The stability of the 1T phase and the transformation to the 2H phase is monitored periodically with UV-Vis spectroscopy and no well-resolved peaks are evident for at least 40 days in storage conditions, protected from atmosphere oxygen and light.

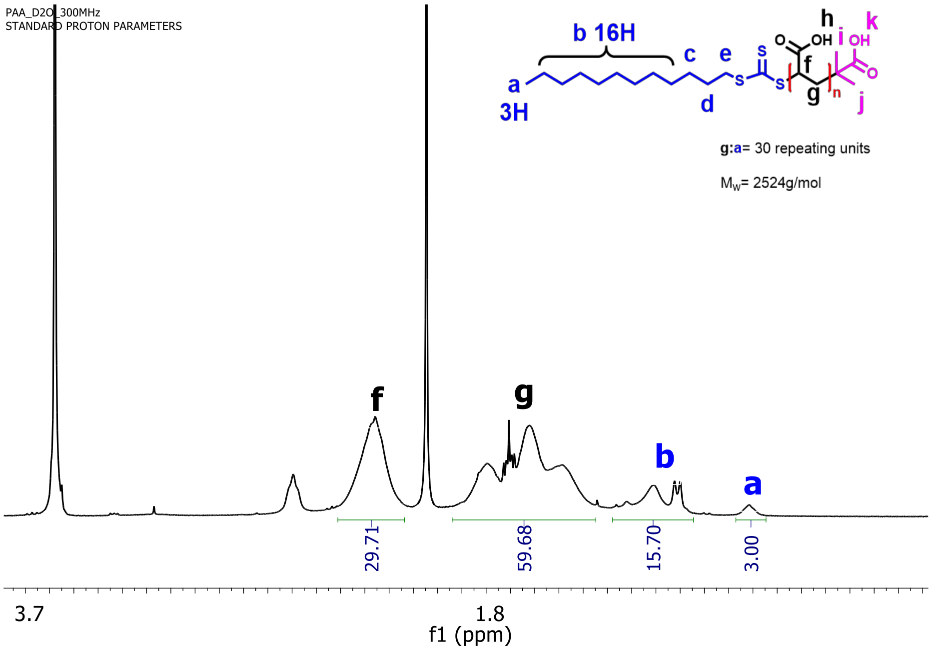
### Synthesis of poly(methacrylic acid methyl ether), PMMA, via reversible addition−fragmentation chain-transfer (RAFT) polymerization

In a 25mL round-bottom flask, the monomer methacrylic acid methyl ether (MMA) (1.5g), the chain-transfer agent (CTA) 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (0.084g, 0.3mmol), the initiator 2,2′-azobis(2-methylpropionitrile) (0.005g, 0.03mmol) and the solvent 1,4-dioxane (7.5mL) were added. Then the reaction mixture was saturated with nitrogen via constant bubbling of high purity gas and placed in a pre-heated oil bath at 70$^0$C. The reaction was left in the oil-bath under stirring for 15h, then cooled to -20$^0$C and subsequently exposed to atmospheric air to terminate the polymerization. The PMMA homopolymer was collected as solid via adding the reaction mixture in a 10-fold volume excess of hexane and dried in a vacuum oven for 48h. The $M_w$ and $M_w/M_n$ values were determined through size exclusion chromatography (SEC) to be 4700 g/mol and 1.19, respectively, through size exclusion chromatography (SEC):



### Synthesis of poly(acrylic acid), PAA, via reversible addition−fragmentation chain-transfer (RAFT) polymerization

In a 25mL round-bottom flask, the monomer acrylic acid (AA) (1.5g), the chain-transfer agent (CTA) 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (0.11g, 0.3mmol), the initiator 2,2′-azobis(2-methylpropionitrile) (0.005g, 0.03mmol) and the solvent 1,4-dioxane (6mL) were added. Then the reaction mixture was saturated with nitrogen via constant bubbling of high purity gas and placed in a pre-heated oil bath at $70^0$C. The reaction was left in the oil-bath under stirring for 15h, then cooled to $-20^0$C and subsequently exposed to atmospheric air to terminate the polymerization. The PAA homopolymer was collected as solid via adding the reaction mixture in a 10-fold volume excess of diethyl ether and dried in a vacuum oven for 48h. The $M_w$ was calculated as high as 2524 g/mol from the $^1$H NMR spectra:



### Synthesis of $MoS_2$-PMMA

In a 150mL round-bottom flask, 26 mL of ce-$MoS_2$ water dispersion (=26mg ce-$MoS_2$), 31.2mL 2-propanol to promote solubilization of PMMA in the aqueous environment and 100mg PMMA were added. The mixture was saturated with nitrogen via constant flow of high purity gas for 30min. The flask was sealed and placed in a pre-heated oil-bath at $60^0$C and stirred for 3d. After, the flask was opened and exposed to atmospheric air to quench any remaining radical species. Then, the reaction mixture was poured into 30mL 1,4-dioxane and placed in the fridge at $3^0$C for 12h. The $MoS_2$-PMMA collected as black precipitate via centrifugation (4.000rpm, 5min) and purified via 3 repeating cycles of dispersing the $MoS_2$-PMMA material in 1,4-dioxane (4mL) via bath sonication and isolating via centrifugation (4.000rpm, 5min) to ensure removal of physiosorbed PMMA chains. Finally, $MoS_2$-PMMA was dried at r.t. in a vacuum chamber.

**Synthesis of $MoS_2$-PAA**

In a 100mL round-bottom flask, 26 mL of ce-$MoS_2$ water dispersion (=26mg ce-$MoS_2$) and 50mg PAA were added. The mixture was saturated with nitrogen via constant flow of high purity gas for 30min. The flask was sealed and placed in a pre-heated oil-bath at $60^0$C and stirred for 3d. After, the flask was opened and exposed to atmospheric air to quench any remaining radical species. Then, the reaction mixture was poured into 30mL 1,4-dioxane and placed in the fridge at $3^0$C for 12h. The $MoS_2$-PAA was firstly collected as black precipitate via vacuum filtration via a PTFE membrane filter with 0.2mm pores and thoroughly washed with 1,4-dioxane and distilled water to remove excess PAA. After, the filter-cake was dispersed in 1,4-dioxane and the $MoS_2$-PAA material was purified via 3 repeating cycles of dispersing the material in 1,4-dioxane (4mL) via bath sonication and isolating via centrifugation (4.000rpm, 5min) to ensure removal of physisorbed PAA chains. Finally, the $MoS_2$-PAA was dried at r.t. in a vacuum chamber.

**Preparation of $MoS_2$-polymer for dispersion stability test**

The isolated covalent $MoS_2$-PMMA and $MoS_2$-PAA ensembles (2 mg) were mixed with each solvent (4 mL) in a glass vial and mildly sonicated in a water bath for 60min. The dispersions were left to settle for 24h and then photographed.

**Complexation of Eu(III) with PAA**

Europium nitrate [$Eu(NO_3)_3•6H_2O$, 99.99%] was dissolved in 5mL distilled water furnishing a Eu(III) concentration of 0.5M (Solution A). Then, 3mL of this solution were diluted with distilled water up to a 3mL volume (Solution B) and stored in a glass vial. The PAA polymer (1mg) was dissolved in 5mL $H_2O$ (Solution C). For the photoluminescence spectroscopy titrations 3mL of the Solution B were titrated by aliquots of Solution C (10mL additions up to total of 100mL, then 20mL additions to reach a total of 300mL). Fluorescence spectra recorded at ambient under 391nm excitation.

**Complexation of Eu(III) with $MoS_2$-PAA**

Europium nitrate [$Eu(NO_3)_3•6H_2O$, 99.99%] was dissolved in 5mL distilled water furnishing a Eu(III) concentration of 0.5M (Solution A). Then, 3mL of this solution were diluted with distilled water up to a 3mL volume (Solution B) and stored in a glass vial. The $MoS_2$-PAA material (1mg) was dispersed in 3mL distilled water (Solution C). For the photoluminescence spectroscopy titrations 3mL of the Solution B were titrated by aliquots of Solution C (20mL additions up to total of 100mL, then 50mL additions to reach a total of 300mL). Fluorescence spectra recorded at ambient under 391nm excitation. During the complexation study the optical absorption at 391nm remained below 0.05, ensuring the absence of inner filter effects.

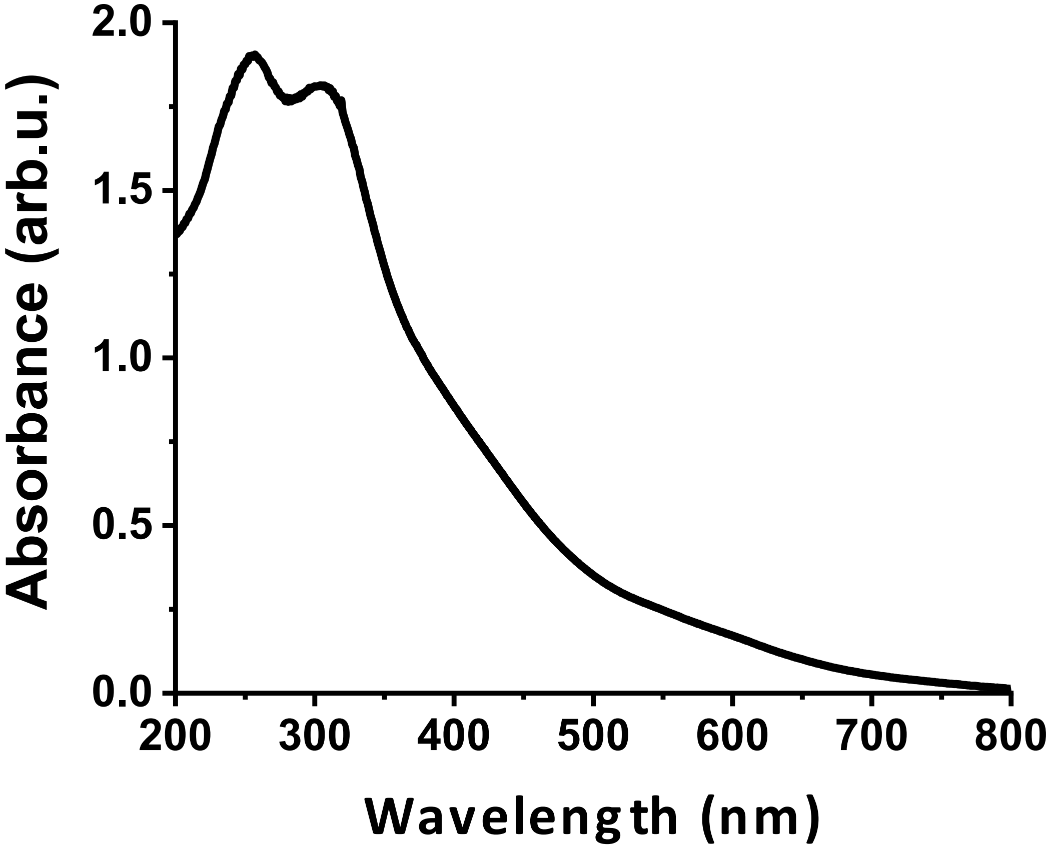


**Figure S1**. UV-Vis spectrum of the diluted as-prepared aqueous suspension of ce-$MoS_2$ exfoliated nanosheets, used for the covalent functionalization with PMMA and PAA polymers.

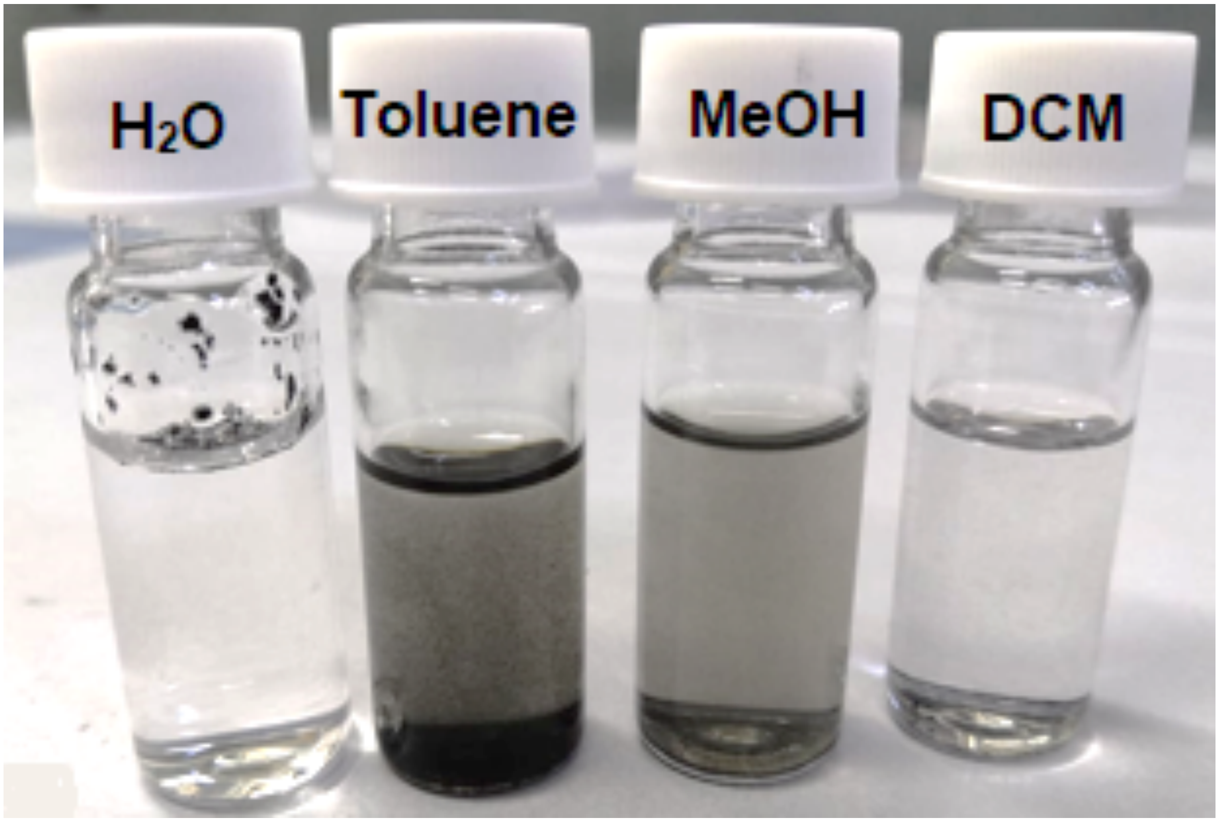


**Figure S2.** Digital photograph of $MoS_2$-PMMA dispersions in water, toluene, methanol and dichloromethane settled for 24h.

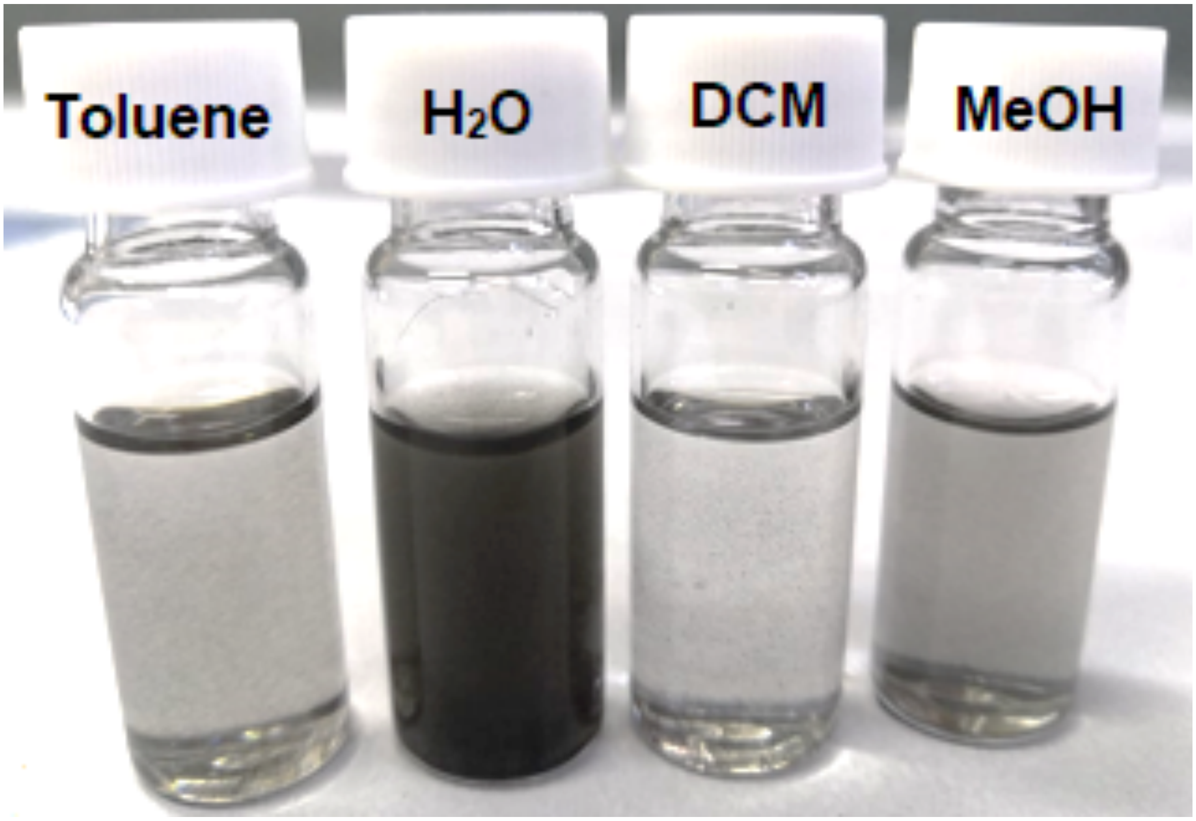


**Figure S3.** Digital photograph of $MoS_2$-PAA dispersions in toluene, water, dichloromethane and methanol settled for 24h.

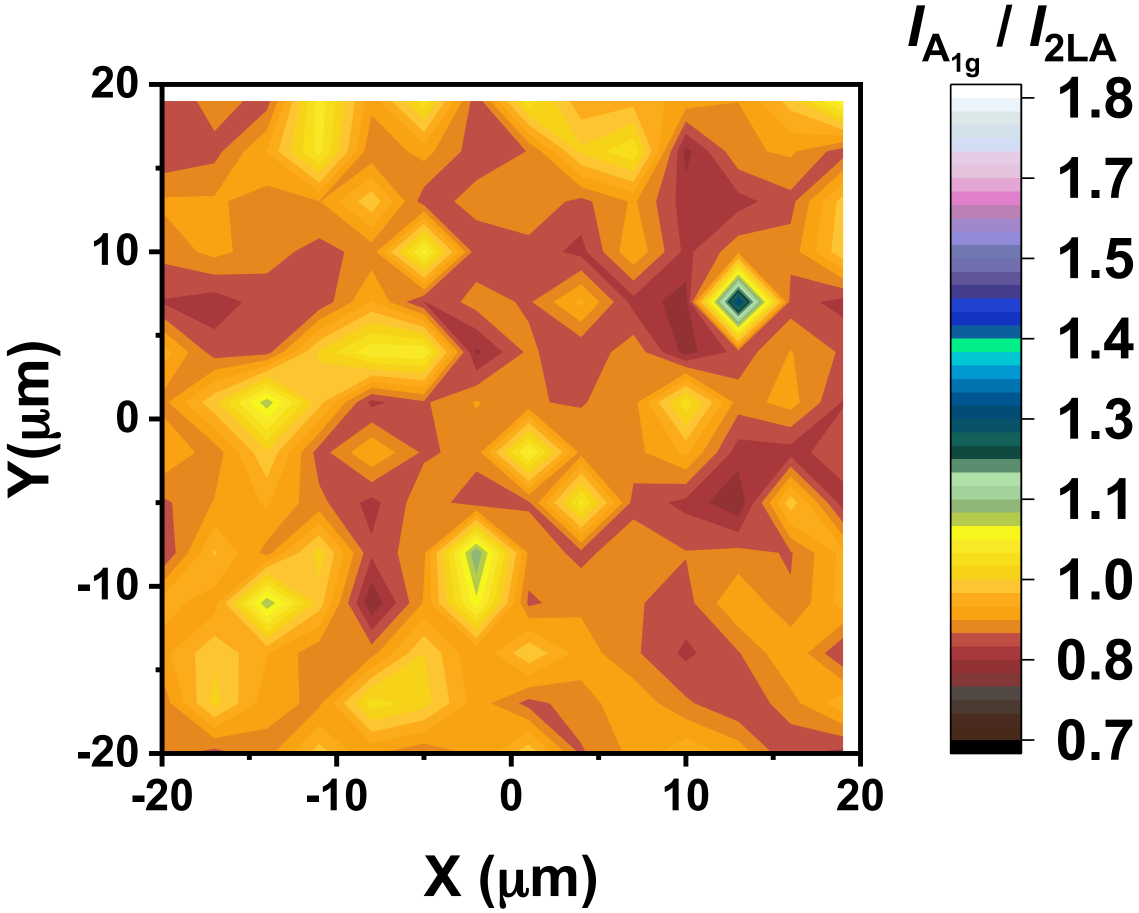


**Figure S4.** Raman intensity ratio maps from a 20 μm x 20 μm area (3 nm step, 196 points/spectra) of *ce*-$MoS_2$. All spectra recorded under 633 nm at low power (0.3 $mW/cm^2$) at ambient conditions.

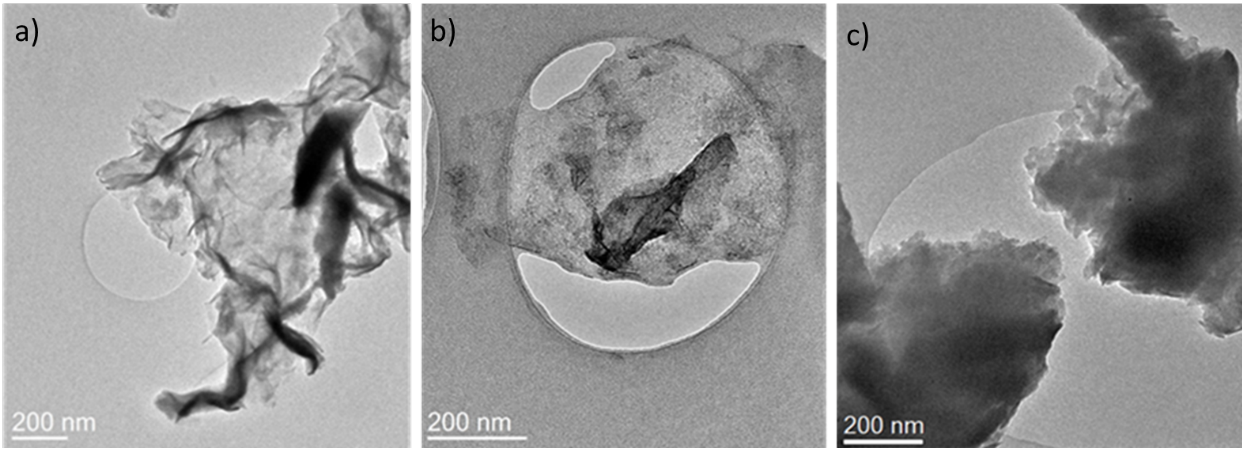


**Figure S5.** TEM images of a) $MoS_2$-PMMA, b) $MoS_2$-PAA and c) *ce*-$MoS_2$. Please note that aggregation on *ce*-$MoS_2$ results on thicker flakes and then a darker appearance can be observed in the TEM image.