

Supporting Information for

Exfoliated sheets of MoS₂ trigger formation of aqueous gels with acute NIR light responsiveness

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Materials: Molybdenum (IV) disulphide (MoS_2 , 99%), Pyrene Butyric Acid, hexafluoro isopropanol (HFIP), all Fmoc protected amino acids, activator (diisopropyl carbodiimide), CTAB, SDS, piperazine, thioanisole, anisole, 1,2-ethanedithiol and trifluoroacetic acid were purchased from Sigma Aldrich. Oxyma, Fmoc-Rink amide MBHA Resin and all solvents were purchased from Merck. Milli-Q Water was used throughout the study.

Synthetic procedure:

Microwave Automated Solid Phase Peptide Synthesizer (Liberty Blue CEM, Matthews, NC, USA) was used to synthesize the peptides (**3**, **4** and **5**). Fmoc-Rink Amide MBHA Resin was placed in the peptide synthesis reactor for 30 minutes with sufficient dimethylformamide for swelling. Fmoc deprotection was completed using 20% piperazine in dimethylformamide containing 10% ethanol in microwave. Each Fmoc amino acid coupling step was achieved by heating in microwave which was activated with diisopropyl carbodiimide (DIC) and Oxyma in DMF. Resin was filtered followed by washing with dichloromethane and allowed to air dry. The peptides were cleaved from the resin by using trifluoroacetic acid/thioanisole/1, 2-ethanedithiol/anisole (90: 5: 3: 2, v/v/v/v) for 3 h at the room temperature. The cleaved peptide-TFA solution was filtered and the filtrate was precipitated drop-wise by adding ice cold (-20°C) diethyl ether. The precipitated product was centrifuged for 10 min at 7000 rpm and further the pellet formed was washed 3 times with cold diethyl ether. Dried peptide was dissolved in minimum amount of 40% acetonitrile/ H_2O containing 0.1% trifluoroacetic acid. The peptide was purified by RP-HPLC using a Waters Semi Preparative binary HPLC system which is fitted with a C18-reverse phase column with an acetonitrile-water gradient containing 0.1%TFA. Fig S15-17 represents the HPLC Chromatograms of purified peptides. Acetonitrile was removed in rotavap, the water containing peptide fractions were frozen and lyophilized to yield a purified peptide powder. Molecular weights of the peptide were confirmed by ESI-MS recorded with Waters, Q-TOF Micromass. For molecule **4**: LCMS (ESI) m/z : $\text{C}_{49}\text{H}_{56}\text{N}_8\text{O}_5$ Calculated 837.4407; Found 837.4341 and for molecule **5**: LC MS (ESI) m/z : $\text{C}_{49}\text{H}_{56}\text{N}_6\text{O}_5$ Calculated 809.4346; Found 809.4000

Self-assembly of Peptides

To ensure homogenous assemblies, the lyophilized powder of pure peptides was treated with hexafluoro isopropanol (HFIP), which removes any preformed aggregates. Briefly, the peptides were dissolved in HFIP, incubated for 10 minutes and then HFIP was removed with flow of nitrogen. The required amount of purified peptide powders were weighed to a screw-capped vial. This was followed

by addition of 40% acetonitrile in water (v/v) containing 0.1% TFA and vortexing to dissolve the solid peptide completely. The solution was incubated at 25 °C for 7 days for their self-assembly. To generate aqueous dispersions, the solutions were centrifuged at 17000 rpm for 30 min. Supernatant was discarded and pellet of peptide assemblies was re-dispersed in fresh water. To remove TFA completely, the process was repeated twice.

Exfoliation Protocol

MoS₂ dispersions were prepared following previously reported protocol.^[1] Briefly, MoS₂ 7.5 mgmL⁻¹ was probe sonicated (QSonica Q700 with point probe at power output of 285 W) in N-Methyl-2-pyrrolidone (NMP) for 1h. It resulted in the formation of black homogeneous dispersion. Further, it was centrifuged (Eppendorf centrifuge 5430 R) for 45 min at 1500 rpm which resulted in black dispersed solution of MoS₂. After centrifugation, aliquot from the upper-half of the solution was pipetted out to a beaker. UV/Vis spectrophotometer (Shimadzu UV-2600) was used for the characterization of the exfoliated MoS₂.

Preparation of MoS₂-peptide dispersion/gels and determination of minimum gelation concentrations (MGCs)

Typically, to dispersions of exfoliated MoS₂ in NMP or DMSO (1.0 ml) in a screw-capped vial with internal diameter (i.d.) of 10 mm, varying concentrations of aqueous nanofiber solution (**3-5**) or surfactants (**1-2**) (9.0 ml) were added (v/v ratio of H₂O and NMP or DMSO was maintained at 10:90). Then the solutions were kept at room temperature without any disturbance. After ca. 8 h, formation of gel was confirmed for **4,5** (Table S1) by inversion of the glass vial, which did not show flow of the solution. The MGCs were recorded (Table S1). For controls, neat NMP/DMSO without MoS₂ were added to aqueous dispersions of **1 – 5** (Table S1). Also, pristine powder of MoS₂ in NMP or DMSO without any sonication was also added to peptide nanofibers as controls.

Transmission Electron Microscopy Imaging:

Peptide solution and MoS₂ containing samples were dropcasted on the carbon-coated copper grids. After ca. 1 min, excess solution was wicked off with the filter paper. For samples with stain, aqueous

solution of uranyl nitrate (2%, w/v) was added and incubated for 3-5 minutes. Samples were then placed in the desiccator under vacuum. TEM micrographs were imaged with a JEOL JEM 2100 with a Tungsten filament at an accelerating voltage of 200 kV.

Lateral flake sizes from TEM

The lateral flake sizes were determined following previously published protocols.^[1-3] From the TEM images in Fig. 3 (in main text) and Fig. S3 and other images, we extensively measured the flake length of more than 100 flakes (the largest distance from any two points on the sheets). The flakes lengths had a broad distribution with lengths ranging from 52 nm to 600 nm with mean $\langle L \rangle = 177$ nm (Fig. S3). Also, it appeared that, typically the flakes had highest population of lateral sizes in the range of 100 nm.

Atomic Force Microscopy (AFM)

Aqueous dispersions of samples (5 μ L) were added on a silicon chip (4" diameter diced silicon wafer cleaned in methanol/ acetone by sonication for 25 min beforehand) and the sample was air dried. AFM images of dried samples were recorded by tapping mode analysis on a Bruker Multimode 8 scanning probe microscope with silicon cantilever (Bruker). For MoS₂-peptide samples, initially 5 μ L was directly placed on a silicon chip and air dried. Densely populated nanofibers were observed (Fig. S6). To remove interfering nanofibers and image MoS₂ sheets, the samples were diluted with water, before drop casting on to the silicon wafers. Notably, dilution is not required for TEM imaging as in the absence of stains, peptide nanofibers are not visible and do not interfere with MoS₂ imaging in most focus ranges. Briefly, the aqueous peptide solutions (1.2 mM) containing MoS₂ was diluted 15 times with water and an aliquot (5 μ L) was placed on a silicon wafer. Afterwards, the wafer was gently washed with water to further remove peptide nanofibers and air dried for imaging.

Raman Spectroscopy

The samples for Raman were prepared by dropcasting (10 μ L) of the dilute dispersion on Silicon substrate and dried in the vacuum desiccator. The Raman spectra were recorded using a WITec Raman Spectroscopy equipped with 1024 X 512 CCD camera. An Argon ion laser (532 nm) was specifically used with an objective of 50X mag. The presence of MoS₂ was confirmed by performing Raman mapping (532nm). Grid with the spacing of 300 nm was used to collect the Spectra. A_{1g} mode of MoS₂ was captured by scanning between the range of 390 and 410 cm⁻¹.

Rheometry

The mechanical properties of the MoS₂-**4** gel were tested using a Rheoplus (Anton Paar, Modular Compact Rheometer 302, Cone plate CP50-1) device equipped with cone plate geometry and distance kept was 0.2 mm. All experiments were done immediately after transferring 1 ml of a prepared 1.2 mM and 4.8 mM of MoS₂-**4** gels and 1.2 mM aqueous solution of nanofibers of **4**. Measurements of storage (G') and loss modulus (G'') were made by varying angular frequency (ω) from 0.1 to 200 rad/s, keeping an oscillatory strain of 0.1%, at a temperature of 25°C.

Fluorescence spectroscopy

Fluorescence spectra were recorded in FS5 spectrofluorometer from Edinburgh instruments at 25°C. The Fluorescence spectra of peptide MoS₂-**4** gel and control nanofibers solution of **4** were recorded with excitation wavelength of 340 nm and emission range from 350 to 550 nm and a slit width of 3 nm for excitation and 2 nm for emission. The concentration was kept at 1.2 mM in both cases.

NIR irradiation

MoS₂-**4** gel (1.2 mM and 2.4 mM) was prepared directly in the quartz cuvette of 2 mm path length following a protocol as mentioned above. NIR laser (804 nm, Femtosecond Pulsed Laser, Coherent Inc.) with continuous beam spot of diameter 8 mm and power density of 1.2 watt/cm² was directed on to the black gel in the inverted cuvette. During irradiation of NIR, the temperature of the black MoS₂-**4** gel was intermittently checked with Thorlab thermometer (the laser was blocked during monitoring of the temperature). After 45 s of irradiation, the gel melted and phase transition occurred from gel to sol. The cuvette containing sol was removed from NIR irradiation and kept in upright position. Re-gelification was observed in ca. 2 min. The process could be repeated for 6 times. For control samples, nanofibers of **4** as solution (2.4 mM) and as gel (60 mM) without MoS₂ was exposed higher power of 3.0 watt/cm² for prolonged time of 10 minutes. The control samples showed minimal change in temperature with time and the gel remained intact.

Thermogravimetric Analysis (TGA)

TGA measurements were performed using Perkin Elmer STA 8000 under N₂ atmosphere with 10 °C min⁻¹ increment of heating rate. For sample preparations, MoS₂-**4** gel sample (4.8 mM) was diluted

with addition of water and filtered under high vacuum using nitrocellulose membrane of 0.22 μm . The black film was washed with water, kept in vacuum oven for drying. The dried mass was used for TGA. For TGA of **4**, nanofiber solution of **4** was lyophilized and resultant dried powder was used. Also, pristine MoS_2 powder was subjected for weight loss experiment by TGA measurement under the same conditions. In case of the exfoliated MoS_2 film, the observed downshift of the oxidation temperature compared to pristine powder can be explained from the smaller size of the sheets.^[2,4] It has been previously observed that size of particles has a role on the oxidation temperature of MoS_2 .^[2,4]

Circular Dichroism Spectroscopy

CD spectra were recorded using JASCO J-1500 Circular Dichroism Spectrometer, Easton, MD, USA. The wavelength range was from 220 nm to 400 nm with scan speed of 200 nm min⁻¹. For CD of MoS_2 -**4** gel, ca. 40 ml was added to demountable cells (0.1 mm path length, Hellma). For the NIR treated sample, MoS_2 -**4** gel (1.2 mM) was made in a cuvette of 2 mm path length. This cuvette was irradiated for 45 s with NIR laser of 804 nm with power output of 1.2 watt/cm². The gel to sol transition occurred as the temperature reached to ca. 57 °C in 45 s. Immediately, CD was recorded by taking 40 ml of sol of MoS_2 -**4** (demountable cells of 0.1 mm path length). For directly heating the same, following similar protocol MoS_2 -**4** gel (1.2 mM) was made in a 2 mm path length cuvette. This cuvette was heated in an electrically controlled digital water bath at 78 °C. After ca. 15 min, the gel to sol transition occurred and immediately 40 ml of the sol was added to the demountable cells (0.1 mm path length, Hellma) to record the CD.

Table S1 Minimum gelation concentration (MGC, mM) of amphiphiles (**1–5**) in water containing 10% DMSO or 10% NMP. The combinations in presence of MoS₂, had either exfoliated MoS₂ or pristine MoS₂ in the organic solvent (DMSO or NMP)

Combinations	State ^a	MGC (mM)
1	S	-
1+ exfoliated MoS ₂	S	-
2	S	-
2+ exfoliated MoS ₂	S	-
3	S	-
3+ exfoliated MoS ₂	S	-
4	G	60 mM
4+ exfoliated MoS ₂	G	1.2 mM
4+ pristine MoS ₂	G	60 mM
5	G	72 mM
5+ exfoliated MoS ₂	G	10 mM
5+ pristine MoS ₂	G	72 mM

^aS: solution (soluble up to 100 mM); G: Gel formation

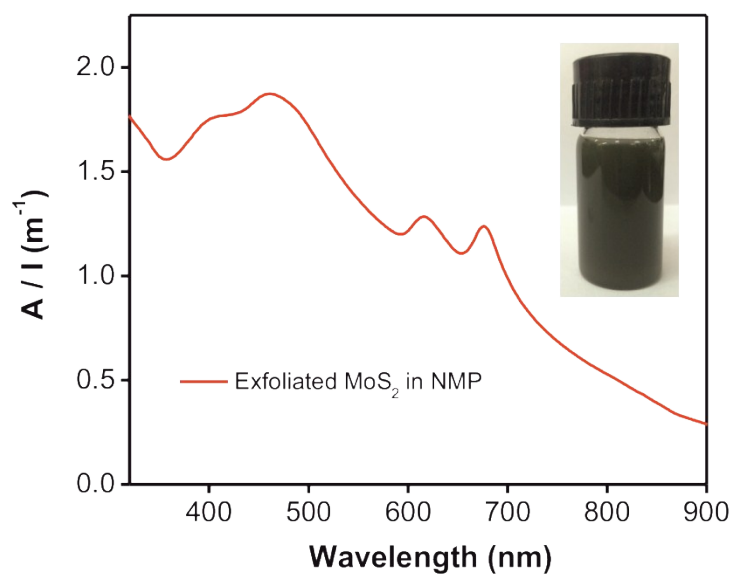


Fig. S1 UV-Vis of exfoliated MoS₂ in NMP. Inset showing vial of exfoliated MoS₂ in NMP.



Fig. S2 Falcon tubes showing the stable redispersion of MoS₂ in the presence of aqueous amyloid nanofibers. Multiple centrifugation and redispersions cycles do not result in loss of dispersions of MoS₂.

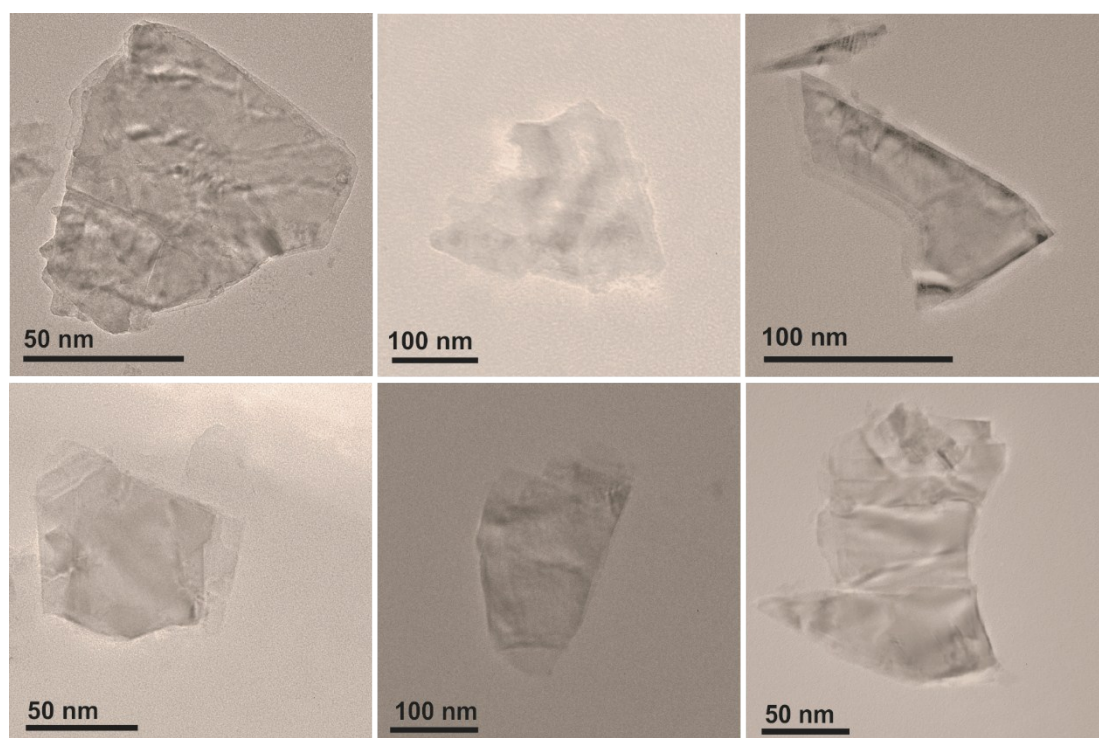


Fig. S3 Additional images viewed under TEM showing thin MoS₂ sheets.

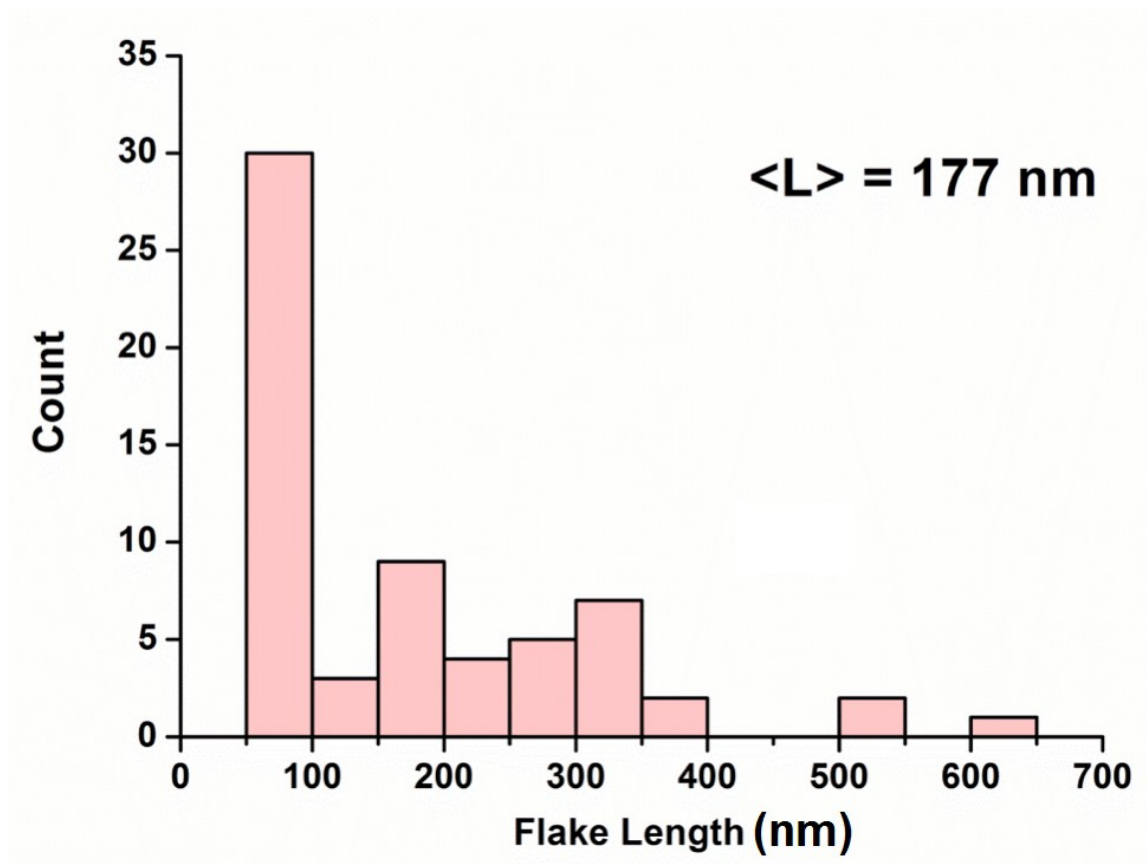


Fig. S4 Histogram of lateral lengths as observed from TEM images. Lengths ranged from 52 nm to 600 nm with mean $\langle L \rangle = 177$ nm.

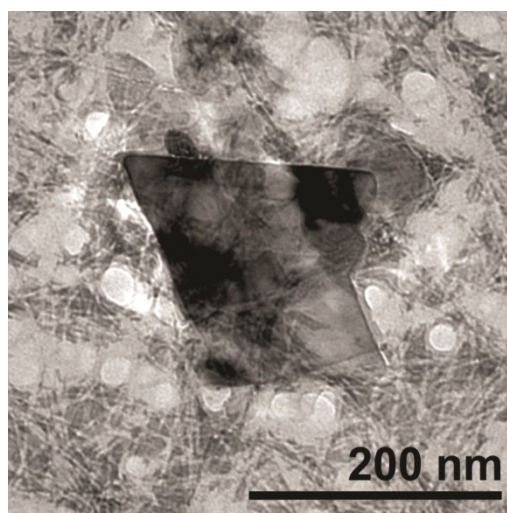


Fig. S5 TEM image of MoS₂-4 in presence of negative stain uranyl nitrate to visualize nanofibers.

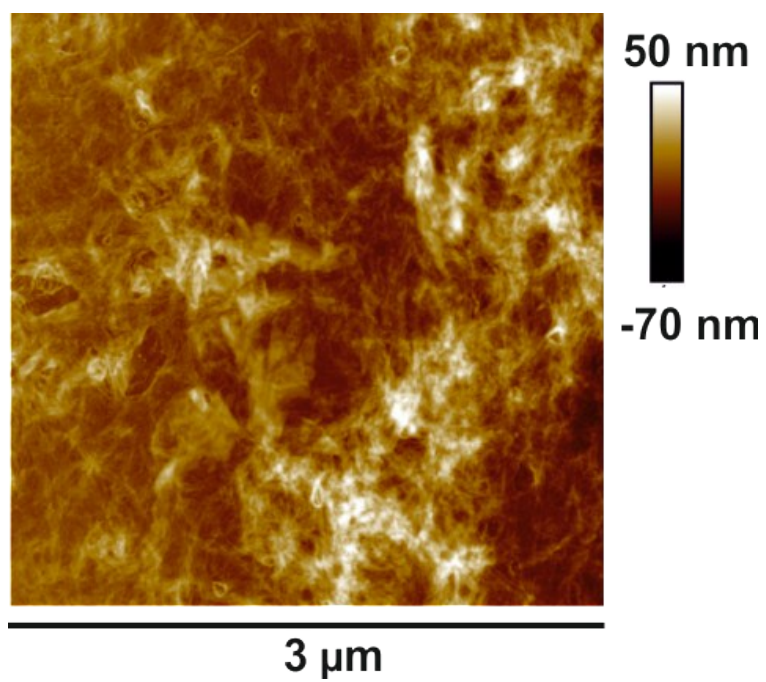


Fig. S6 AFM image of the sample when MoS₂ incorporated hydrogel (MoS₂- 4) was directly drop casted on the silicon substrate.

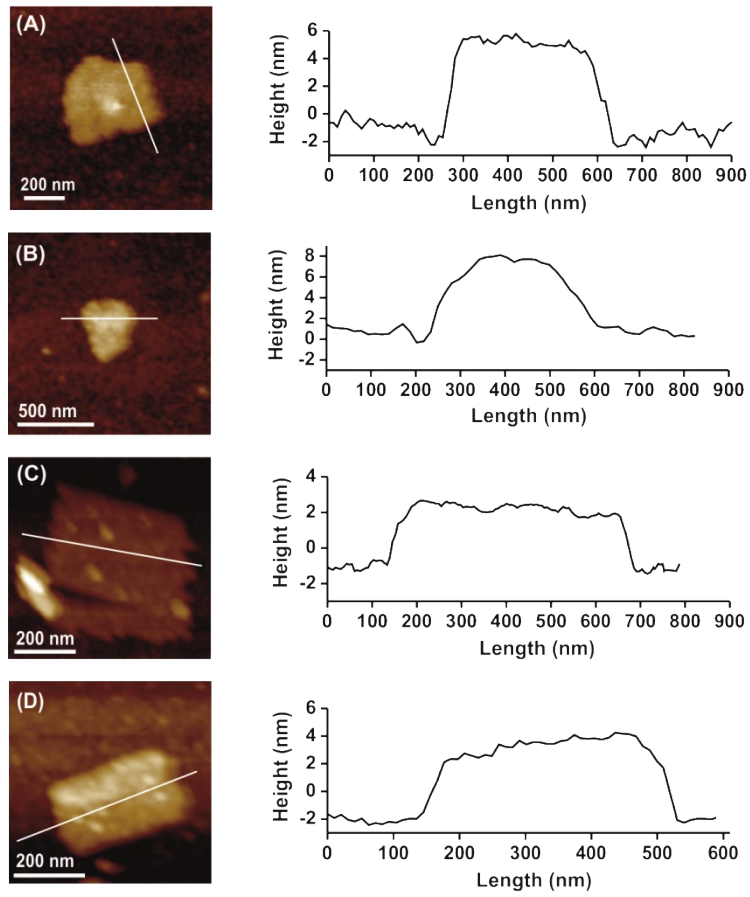


Fig. S7. (A-D) Library showing AFM images of MoS₂ flakes. Corresponding, line analysis representing the height profiles of MoS₂ flakes A-D (marked with white lines) respectively.

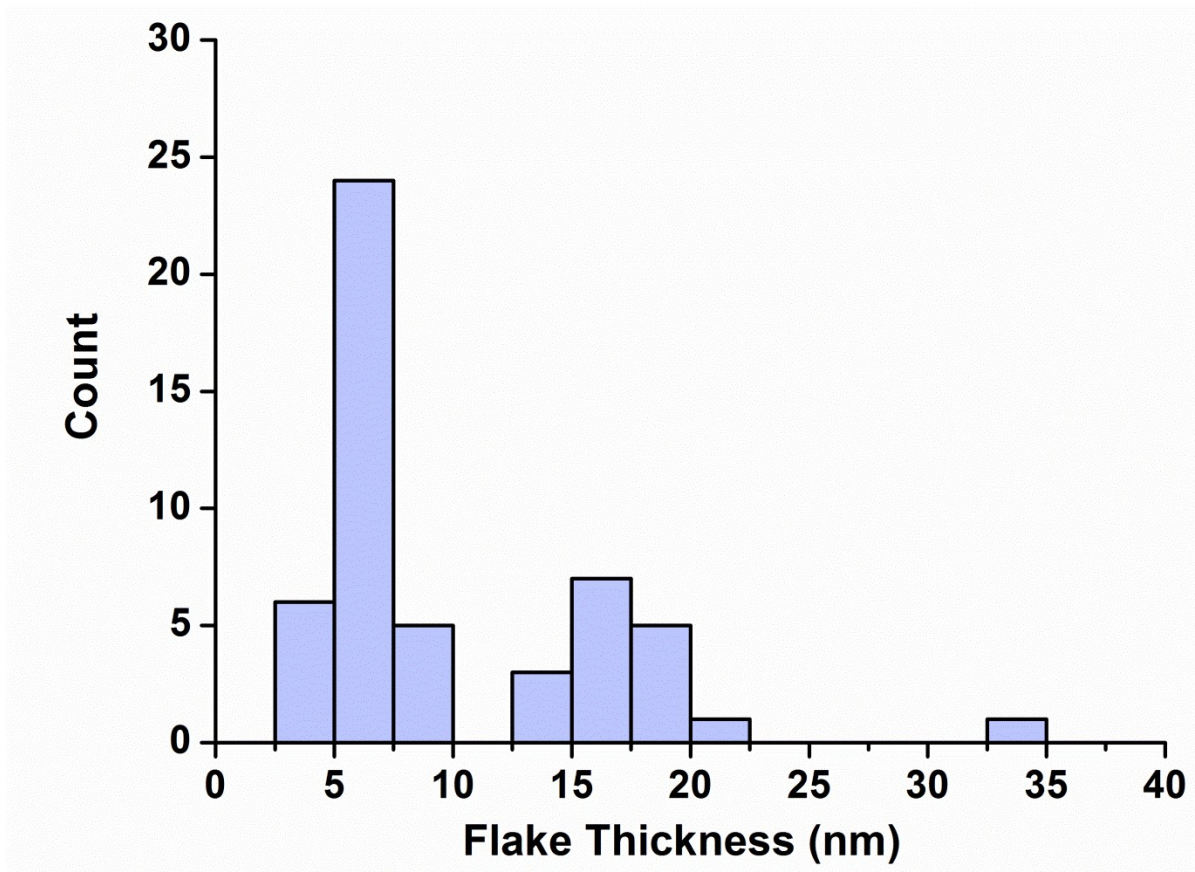


Fig. S8 A Histogram of flake thickness as observed from AFM.

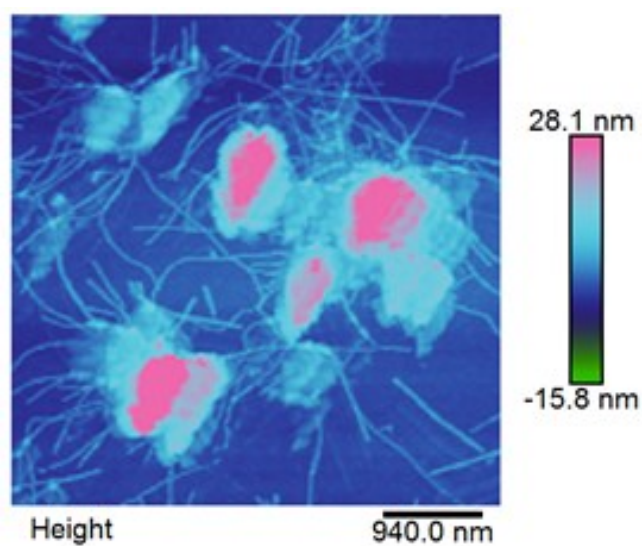


Fig. S9 Colour coded AFM

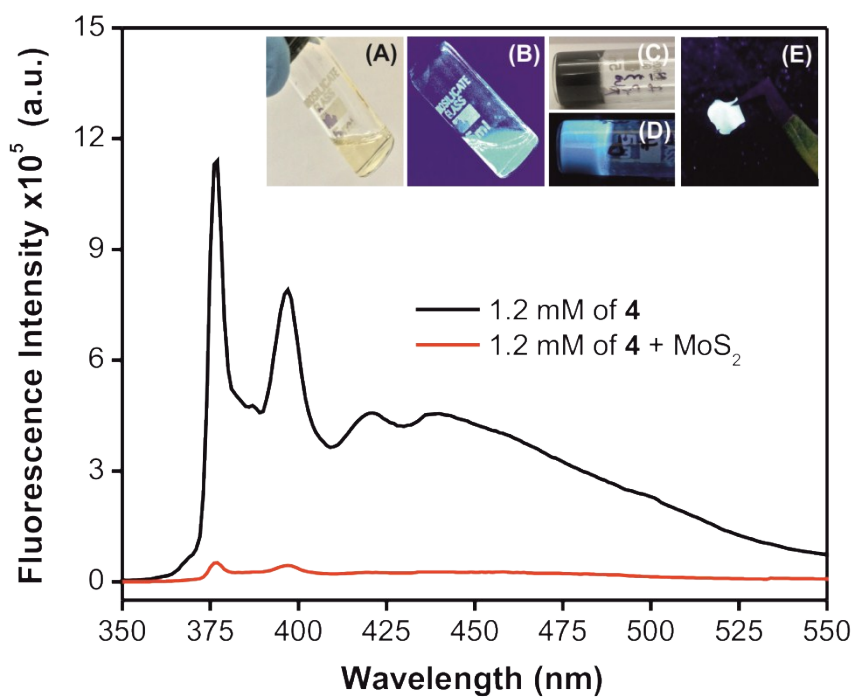


Fig. S10 Fluorescence spectra of nanofiber solution of **4** (black trace) and gel of MoS₂-**4** (red trace). Insets showing photographs of nanofiber solution of **4** under (A) visible light and (B) UV light, photographs of gel of MoS₂-**4** under (C) visible light and (D) UV light. (Wavelength of UV Light = 365 nm, 6 watt) (E) MoS₂-**4** hydrogel dried film imaged under UV light after drying for 15 days.

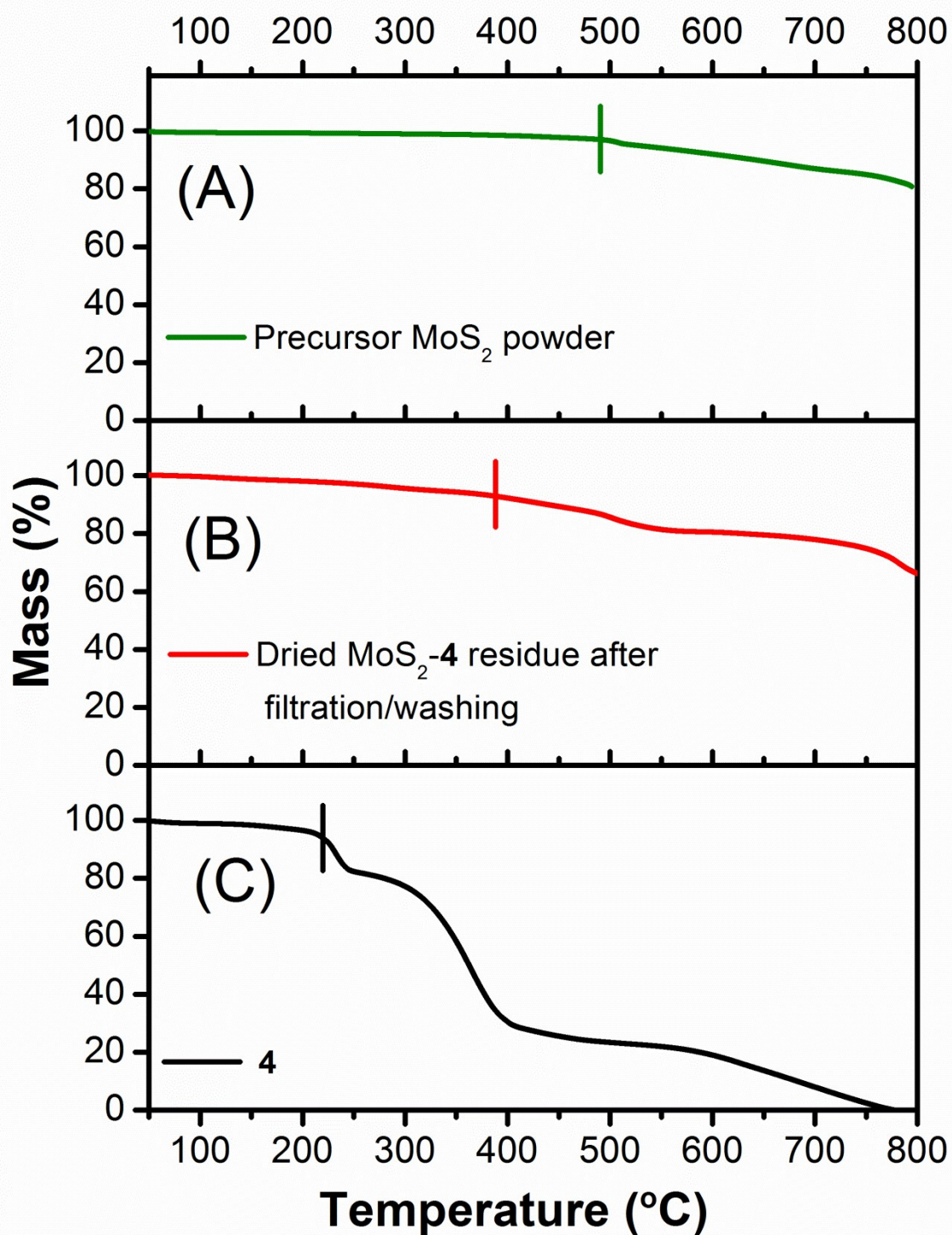


Fig. S11 Thermo gravimetric analysis plot showing decomposition of (A) precursor MoS₂, (B) dried residue of MoS₂ obtained after filtration and washing of MoS₂-4 gel, and (C) lyophilized powder of pure 4.

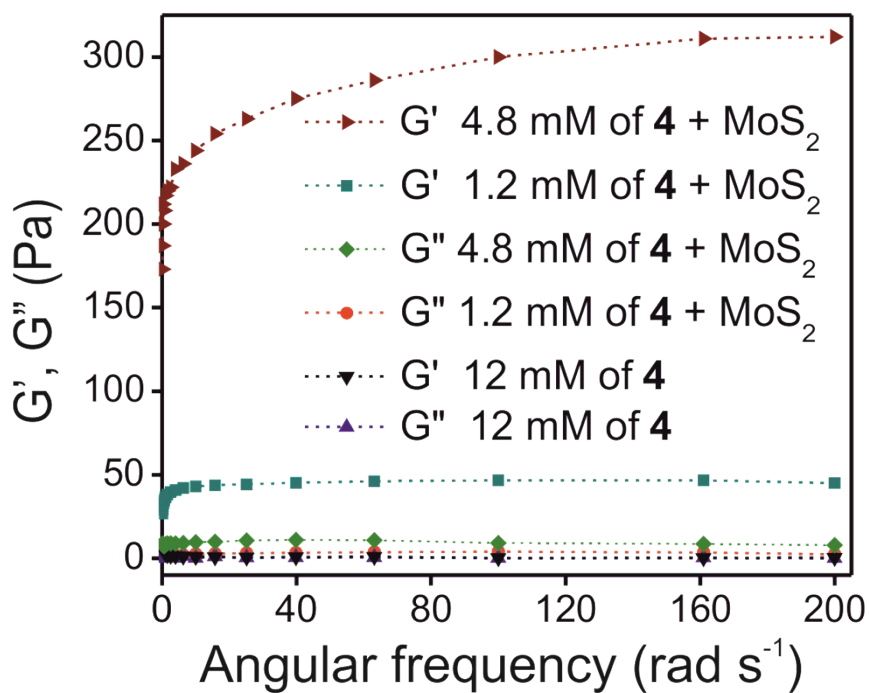


Fig. S12 Frequency dependence of storage (G') and loss modulus (G'') for MoS_2 -**4** gels (1.2 mM and 4.8 mM) and nanofibers of **4** (12 mM) at a strain of 0.1%.

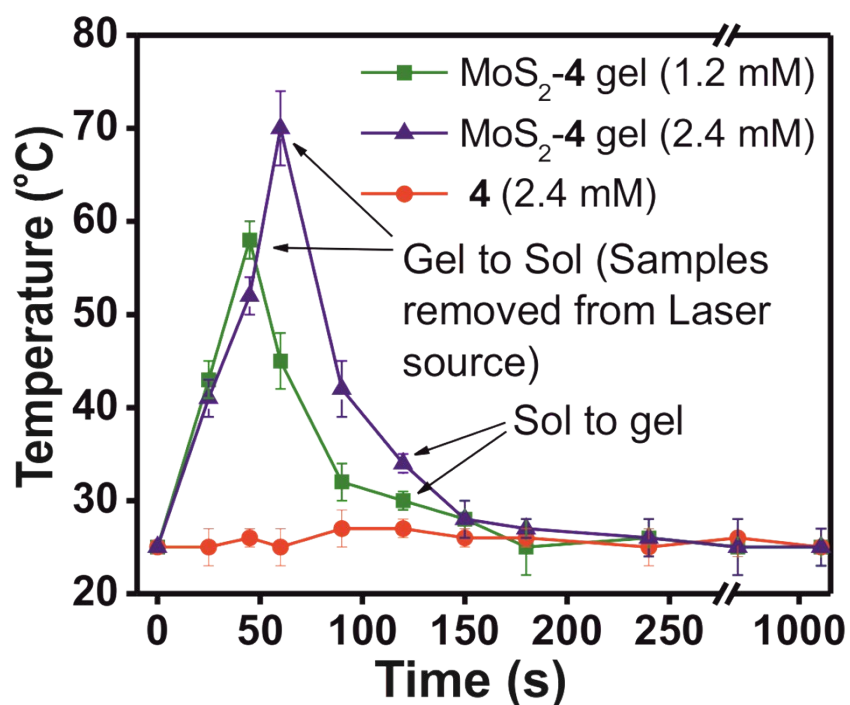


Fig. S13 Temperature versus time of NIR laser irradiation (804 nm) on MoS_2 -**4** gel (1.2 mM and 2.4 mM) and nanofibers of **4** (2.4 mM).

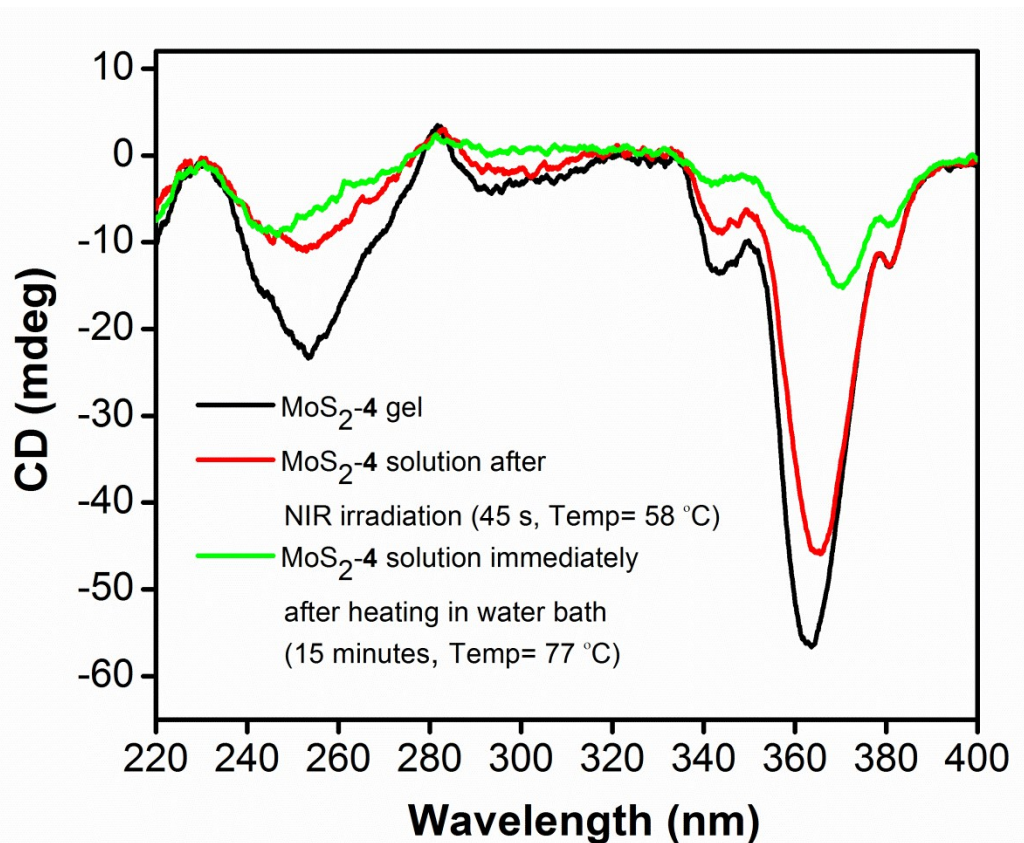


Fig. S14 (Red trace) CD spectrum of MoS₂-4 solution immediately recorded after NIR irradiation of the corresponding gel for 45 s (temperature of cuvette was 58 °C). (Green trace) CD spectrum of MoS₂-4 solution immediately recorded after heating the corresponding gel at 77 °C in water bath. (Black trace) CD spectrum of MoS₂-4 gel.

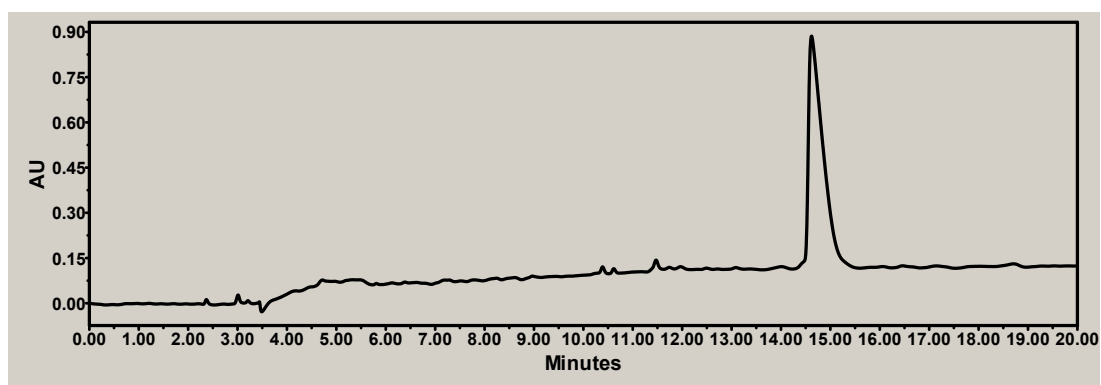


Fig. S15 HPLC chromatogram of **3** (C18 Column, linear gradient from 65 to 85 % in CH₃CN in 20 min).

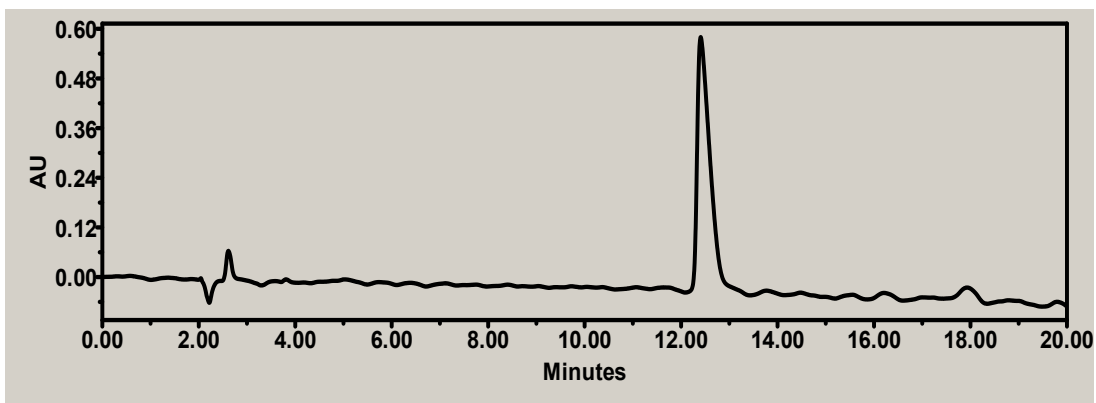


Fig. S16 HPLC chromatogram of **4** (C18 Column, linear gradient from 65 to 85 % in CH₃CN in 20 min).

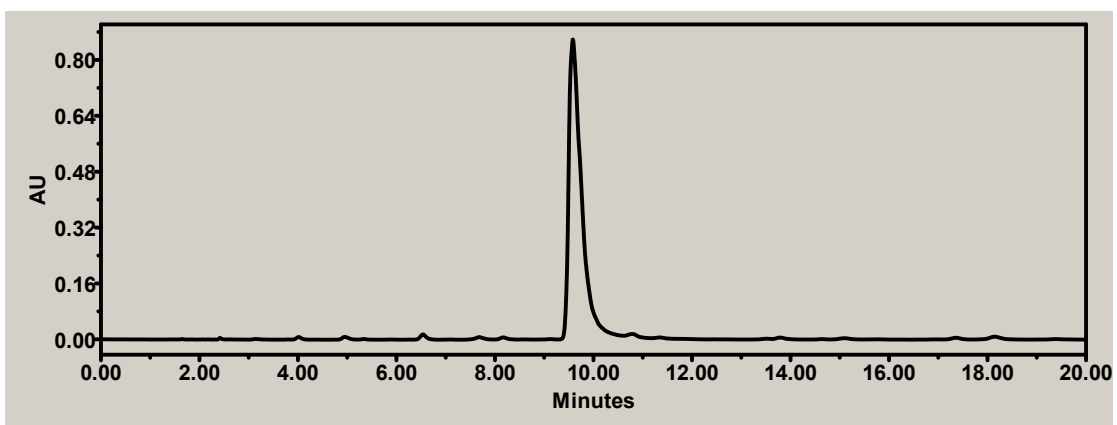


Fig. S17 HPLC chromatogram of **5** (C18 Column, linear gradient from 65 to 85 % in CH₃CN in 20 min).

WATERS, Q-TOF MICROMASS (LC-MS)

NIDHI PY-R 5 (0.171) AM (Top,10, Ar,5000.0,556.28,0.70,LS 10); Sm (Mn, 2x3.00); Sb (1,40.00); Cm (4:6-10:15)

SAIF/CIL,PANJAB UNIVERSITY,CHANDIGARH

1: TOF MS ES+
9.06e3

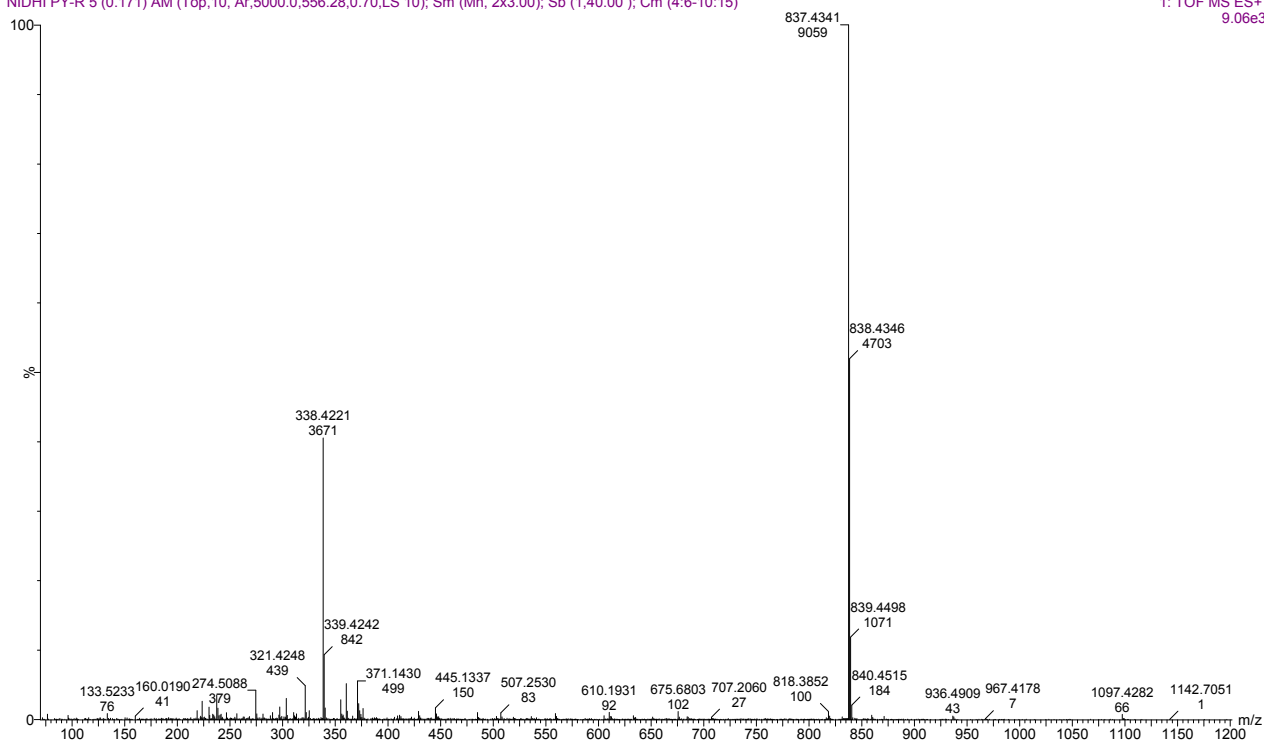


Fig. S18 Mass spectrum confirming the synthesis of 4.

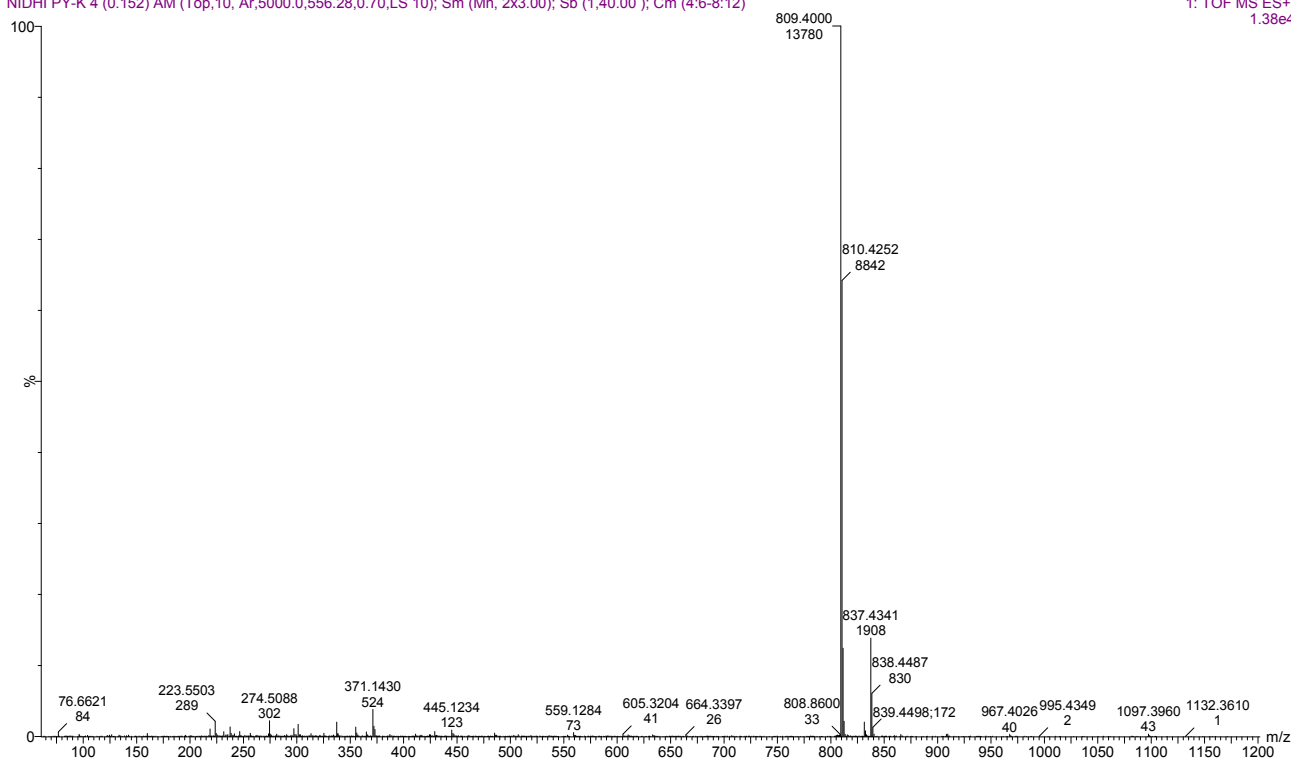


Fig. S19 Mass spectrum confirming the synthesis of **5**.

References

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