## **Electronic Supporting Information**

## Unexpected Optical Limiting Properties from MoS<sub>2</sub> Nanosheets Modified by Semiconductive Polymer

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## **Experimental methods**

*Materials and experiments:* All chemical reagents were of analytical grade and were obtained commercially. MoS<sub>2</sub> powder (300 mg, Aladdin Reagent Inc.) was poured to 100 mL chloroform in a 500 mL bottle. Then 20 mg of poly(3-hexylthiophene) (P3HT) was added under the condition of stirring. The sealed bottle was sonicated for 8 h, and then the dispersion was centrifuged at 3000 rpm for 10 mins to remove unexfoliated flakes. The supernatant was collected and UV/Vis spectra were measured to evaluate dispersion concentration. The dispersion centrifuged at 3000 rpm was then centrifuged at 12000 rpm for 10 mins to remove excess P3HT, and the aggregates were redispersed in chloroform or other solutions for the subsequent characterization. We have frequently dried the samples in ovens heated to ~80 degrees for one hour, treatment of which did not remove the polymer from the hybrid.

*TEM characterization:* TEM images are obtained using a FEI Tecnai  $G^2$  F30 Twin microscope with a LaB6 filament operated at 300 kV. The samples were prepared by drop-casting samples dispersed in chloroform onto holey carbon grids.

*XRD characterization:* XRD was performed on a PANalytical X'pert PRO using Bragg–Brentano geometry. The samples were prepared by drop-casting concentrated solutions onto silicon substrates. XRD patterns are compared to those of hexagonal MoS<sub>2</sub> (JCPDS card No. 37-1492).

*UV/Vis absorption spectra:* The collection of UV/Vis absorption spectra was performed on a TU-1810 spectrophotometer (Beijing Purkinje General Instrument, China).

*Raman characterization:* Raman spectra were measured with a Renishaw InVia Raman microscope at room temperature with a 633 nm line laser as the excitation source.

*Fluorescence measurement:* The steady-state fluorescence spectra were collected on a Perkin–Elmer LS 55 fluorescence spectrometer. The absolute quantum yield was obtained on a FLS 920 fluorescence spectrometer (Edinburgh Instrument, UK).

*Fluorescence lifetime measurement:* The fluorescence lifetime measurements were carried out on a FluoTime 200 (PicoQuant GmbH, Germany) TCSPC time-resolved

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fluorescence platform, equipped with a nanosecond pulsed LED (Pulse width<750 ps) at 464 nm as the excitation source.

*Z-scan setup*: We refer the readers to the supporting information for the detailed schematic setup (Figure.S7) and explanations therein. Briefly, for a nanosecond *Z*-scan measurement, 5 ns (FWHM), 532 nm laser pulses with a repetition rate of 10 Hz from a frequency-double Q-switched Nd:YAG laser (Continuum, Model Surelite SL-I-10) was used as the light source. Two corresponding pyroelectric detectors (Laser Probe, RJ-735; with RJ7620 dual channel power meter) were used to measure changes in laser transmission. The samples were placed in quartz cells with thickness of 2 mm.



**Figure S1.** Photographs of dispersions for  $P3HT-MoS_2$  nanohybrid in chloroform, carbon tetrachloride (CCl<sub>4</sub>), tetrahydrofuran (THF), toluene (TOL) and o-dichlorobenzene (ODCB).



Figure S2. Photographs of dispersions for P3HT in chloroform,  $MoS_2$  in the mixture of water and ethanol and P3HT-MoS<sub>2</sub> nanohybrid in chloroform.



**Figure S3.** UV/Vis spectra of of P3HT-MoS<sub>2</sub> nanohybrid in (a) carbon tetrachloride, (b) tetrahydrofuran, (c) toluene, (d) o-dichlorobenzene.



Figure S4. XRD patterns of (a) bulk MoS<sub>2</sub> and (b) P3HT-MoS<sub>2</sub> nanohybrid.



**Figure S5.** (a) AFM images and (b) height profiles of P3HT-MoS<sub>2</sub> nanohybrid, (c) AFM images of P3HT casted on Si, (d) STEM images of P3HT-MoS<sub>2</sub> nanohybrid.

As shown in Figure S5a and Figure S5b, the obtained P3HT-MoS<sub>2</sub> nanohybrid have a uniform distribution of lateral dimension between 50 nm to 400 nm. The thickness of the MoS<sub>2</sub> sheets were around 2–4 nm measured from AFM image profile. However, the AFM images of P3HT casted on Si (Figure S5c) show irregular morphology, which is different from the MoS<sub>2</sub> flakes in Figure S5a. From the STEM images of P3HT-MoS<sub>2</sub> nanohybrid in Figure S5d, we can see that the MoS<sub>2</sub> sheets are very thin, in accordance with the AFM images.



**Figure S6.** (a) XPS survey spectrum of P3HT-MoS<sub>2</sub> nanohybrid. (c-d) XPS spectra of C 1s, S 2p and Mo 3d for P3HT-MoS<sub>2</sub> nanohybrid.

The XPS survey spectrum shows that Mo, S, and C elements coexisted in the film. The XPS peak for C 1s at 284.4 eV is ascribed to adventitious carbon from P3HT on the MoS<sub>2</sub> nanosheets<sup>1</sup>. The XPS spectrum of the S 2p region at 163.5 and 161.9 eV can be ascribed to S  $2p_{1/2}$  and  $2p_{3/2}$ . A typical high resolution XPS spectrum for the high resolution spectrum of Mo 3d, two peaks at 232.2 and 229.0 eV are attributed to Mo(+4)  $3d_{3/2}$  and Mo(+4)  $3d_{5/2}$ , respectively<sup>1-2</sup>.



**Figure S7.** Open aperture Z-scan data and theoretical fit curves using 4 ns pulses at 532 nm for the P3HT-MoS<sub>2</sub> nanohybrid at different incident laser energy with same linear transmittance of 0.58.  $T_{norm}$  is the measured transmittance normalized by the linear transmittance of the sample.



**Figure S8.** Mott–Schottky plots of  $MoS_2$  nanosheets in 0.5 M  $Na_2SO_4$  solution under dark conditions. There is a positive slope in the linear region of the plot, indicating an n-type characteristic. From which we can get the CB of  $MoS_2$  nanosheets is -3.8 eV and the VB is -5.6 eV according to the UV-vis spectrum<sup>3</sup>. The energy levels of P3HT was reported elsewhere<sup>4</sup>.



Figure S9. Schematic representation of the Z-scan experimental arrangement.

Z-scan measurement<sup>5</sup>: For a nanosecond Z-scan measurement, 5 ns (FWHM), 532 nm laser pulses with a repetition rate of 10 Hz from a frequency-double Q-switched Nd:YAG laser (Continuum, Model Surelite SL-I-10) was used as the light source. The spatial and temporal profiles of the laser pulses presented an approximately Gaussian distribution. The output laser beam with nearly Gaussian distribution was split into two beams: a reference beam to monitor energy fluctuations and a strong beam in a tightly focused geometry. The quartz cell was placed on a translation stage controlled by a computer that moved along the z-axis with respect to the focal point of a 410 mm convex lens. The beam waist radius equal to 20  $\mu$ m with a Rayleigh length z<sub>R</sub> of 2362 µm. This Rayleigh length was much larger than the thickness of the sample. Two corresponding pyroelectric detectors (Laser Probe, RJ-735; with RJ7620 dual channel power meter) were used to measure changes in laser transmission. Under the openaperture configuration, the aperture placed before the detector was kept open and the nonlinear absorption of the samples was measured. The other part of laser beam was simultaneously measured by another detector with a partially closed aperture set in front of it, which is the close-aperture configuration. The intensity change detected herein contained both nonlinear absorption and nonlinear refraction. The Z-scan curve, which is the normalized transmittance as a function of the sample position, was measured with and without an aperture in the far field. Herein, we used normalized transmittance, which equals to the ratio of nonlinear and linear transmittance, as a standard to study the NLO properties pentacene derivatives. The samples were placed in quartz cells with thickness of 2 mm, mounted on a translation stage that was

controlled by a computer to move along the z axis with respect to the focal point. In this measurement, normalized transmittance of 1.0 indicates that the material exhibits no NLO behavior. When the sample exhibits saturable absorption, normalized transmittance above 1.0 will be observed. In contrast, the normalized transmittance below 1.0 indicates that the sample exhibits reverse saturable absorption. For optical limiters, the measured curves would exhibit valleys at the focus and the deeper the valley, the stronger the optical limiting performance of the material.

In recent Z-scan measurements on graphene and transition metal dichalcogenides (TMDs), both saturable (SA) or reverse saturable absorption (RSA) phenomena have been reported<sup>6</sup>. Based on the reported work, we applied a two-process equation to fit the Z-scan curves<sup>6a, 7</sup>:

$$\alpha = \frac{\alpha_0}{1 + \frac{I}{I_s}} + \beta I$$
 equation (1)

where  $\alpha_0$ , *I* and  $\beta$  are the linear absorption coefficients, incident laser intensity, and effective nonlinear coefficient, respectively. *I*<sub>s</sub> is the saturation intensity (intensity at which the linear absorption drops to half of its original value).

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