Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Porphyrin Chemically Modified MoS_2 Quantum Dots for Solid-State Broadband Optical Limiters

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Experimental section

1. Materials

All chemicals were of reagent grade, purchased from Aldrich and used without further purification. Organic solvents were purified, dried, and distilled under dry nitrogen (N_2).

2. Characterization

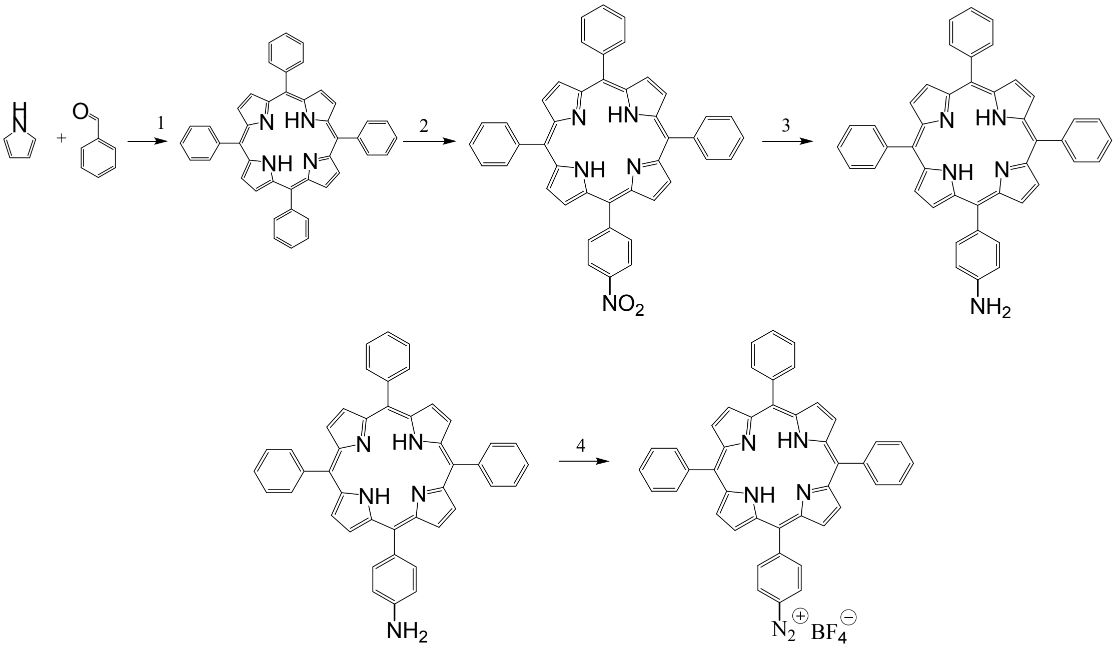
The ultraviolet-visible (UV-Vis) absorption spectra were recorded on Shimadzu UV-2450 spectrophotometer. Fourier Transform infrared spectroscopy (FTIR) were obtained by using potassium bromide pellets on a Nicolet Nagma-IR 550 spectrophotometer. Transmission electron microscope (TEM) images were taken with a JEOL-2100 (Japan, JEOL Ltd). Atomic force microscopy (AFM) were performed on a Multimode Nanoscope VIII instrument (Bruker). Raman spectra were recorded on an Invia/Reflrx Laser Micro-Raman spectrometer (Renishaw, England) with excitation laser of 633 nm. X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos AXIS HSi spectrometer with a monochromatized Al KR X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV.

3. Z-scan measurements

The NLO and OL performances of the samples were investigated through a standard open-aperture from a Q-switched Nd:YAG laser operating at 1064 nm and its second harmonic 532 nm with the 6 ns pulse. The laser beam was tightly focused with a 15 cm focus lens and the repetition rate were set to 2 Hz.

4. Materials Synthesis

TPP-NH$_2$ and TPP-$N_2^+BF_4^-$ was synthesized according to literature procedures.[1,2]



Scheme S1. Reagents and conditions: 1) Propionic acid, reflux; 2) $NaNO_2$, trifluoroacetic acid; 3) $SnCl_2$, conc. HCl(aq), 80 °C; 4) HBF_4, isoamyl nitrite, CH_3COOH.

4.1 Synthesis of TPP

First, freshly distilled pyrrole (7 mL, 0.1 mol) and benzaldehyde (10.6 g, 0.1 mol) were added to reflux flask, subsequently propionic acid (200 mL) was added and the whole mixture was refluxed for 45 min at 135 °C. The refluxed solution was cooled to room temperature overnight. Furthermore, the refluxing solution was filtered and washed with hot ethanol and hot water. Purification by dry column chromatography using silica gel as a stationary phase and $CHCl_3$ as mobile phase. ^1H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 8H), 8.26-8.17 (m, 8H), 7.82-7.71 (m, 12H), -2.78 (s, 2H).

4.2 Synthesis of TPP-NO$_2$

TPP (3.0 g, 4.88 mmol) was dissolved in trifluoroacetic acid (60 mL). Sodium nitrite

(606 mg, 8.78 mmol) was added. The mixture was stirred exactly 3.5 min. The resulting solution was transferred to a beaker containing 150 mL of distilled water and extraction with dichloromethane. The organic layer was washed with saturated aqueous $NaHCO_3$, dried over sodium sulfate and solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (dichloromethane/ petroleum ether=1:1) to afford 1.91 g (59%) pure product TPP-NO_2 as a purple powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95-8.83 (m, 6H), 8.75 (d, 2H), 8.65-8.61 (m, 2H), 8.42-8.37 (m, 2H), 8.23 (dd, 6H), 7.84-7.72 (m, 9H), -2.76 (s, 2H).

4.3 Synthesis of TPP-NH_2

TPP-NO_2 (990 mg, 1.5 mmol) was dissolved in concentrated hydrochloric acid (45 mL) and while stirring, tin(II) chloride (3.3 g, 15 mmol) was carefully added. The final mixture was heated to 80 °C for 2 h under nitrogen before being poured into cold water (150 mL). The aqueous solution was neutralized with ammonium hydroxide until pH 8. The aqueous solution was extracted with dichloromethane until colorless. The organic layer was dried over sodium sulfate and then concentrated under vacuum. The residue was purified on a plug of silca gel using dichloromethane for elution. yielding 55.3 mg (54%) of TPP-NH_2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (t, 2H), 8.86 (s, 6H), 8.32-8.18 (m, 6H), 8.04-7.98 (m, 2H), 7.85-7.69 (m, 9H), 7.11-7.00 (m, 2H), 3.98 (s, 2H), -2.72 (s, 2H).

4.4 Synthesis of TPP-$N_2^+BF_4^-$

0.5 mL (1.59 mmol) HBF_4 (in 50 wt% H_2O) were added to 750 mg (1.2 mmol) TPP-NH_2. Subsequently, 50 mL acetic acid were added and 0.5 mL (0.75 mmol) isoamyl nitrite also dissolved in 25 mL acetic acid were slowly dropped to the green solution. The reaction mixture was quenched with 50 mL diethyl ether after 10 minutes and stored at -22 °C for 6 hours. The green solid was filtered off over a 0.2 μm pore filter and washed with diethyl ether yielding 98 % (855 mg, 1.2 mmol) of the porphyrin diazonium salt. IR (KBr): 2260 cm^{-1} (N_2^+ group); MALDI-TOF: m/z 615 $[TPP+H]^+$, 631 $[TPP\text{-}NH_2]^+$.

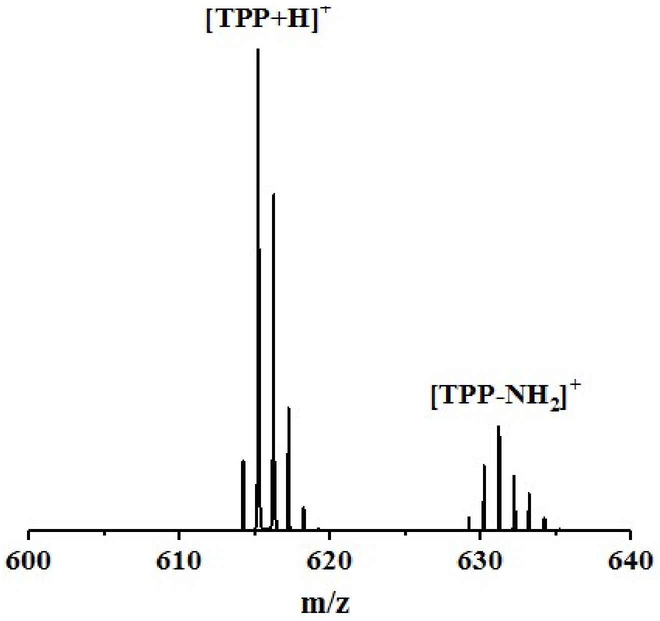


Figure S1. MALDI MS spectrum of TPP-$N_2^+BF_4^-$

4.5 Preparation of MQDs

Typically, 5 g of MoS_2 crystals and 500 mL of DMF were added in beaker and kept sonication for 4 h with an output power of 240 W to exfoliate MoS_2 crystals. The black dispersion was settled overnight and then the top 4/5 was decanted carefully into round-bottomed flask and kept refluxing at 140 °C for 6 h. Afterwards, the resulting suspension was cooled down and settled for several hours or centrifuged for 5 min at low speed (2000~3000 rpm) to separate the supernatant and precipitation. The light yellow supernatant was MQDs solution. In order to remove the excessive solvent and get the solid MQDs sample, part of supernatant was evaporated firstly under vacuum at 90 °C, then the residual solution was dialyzed using dialysis membranes of 500 Da molecular weight cut-off against pure water for 3 days. In order to avoid quantum dots agglomeration, the collected MQDs in aqueous solution was further freeze-dried at -30 °C to obtain 5.8 mg of gray-black MQDs.

4.6 Preparation of MQDs-TPP

Solution phase of MQDs was obtained by the sonication and solvothermal treatment of 5 g MoS_2 crystals in 500 mL DMF. Repeat above-mentioned experiment twice, the excessive solvent in three beakers was removed under vacuum at 90 °C to keep the volume of MQDs solution in 30 mL. Then the resulting suspension was cooled down and a solution of porphyrin diazonium salt (100 mg, 0.14 mmol) in 10 mL DMF was added dropwise with dropping funnel under nitrogen atmosphere, the reaction was further stirred for 24 h at 0 °C to allow the diazonium salt and MQDs to react completely. After the reaction was finished, the resulting dispersion was dialyzed (molecular weight cut-off 500 Da) against DMF for 4 days to remove excess porphyrin diazonium salt, and then continued to be dialyzed against deionized water for additional 3 days. Finally, the dispersions of MQDs-TPP collected by dialysis were further freeze-dried at -30 °C to obtain a purple product.

4.7 Preparation of PMMA-based films

The preparation of PMMA-based films describe as follows: Firstly, MQDs, TPP and MQDs-TPP were dissolved in N,N-Dimethylformamide (DMF) at a concentration of 1 g L^{-1}, then different amount of the samples were added into a cyclohexanone solution of PMMA (100 g L^{-1}) for obtaining the PMMA-based films with similar linear transmittances. The final mixture was sonicated for 30 min and then transferred to the petri dish with a diameter of 6 cm. The residual organic solvent was removed by high vacuum at 60 °C for 72 h. Finally, the PMMA-based solid-state films were taken out carefully from the petri dish by tweezer before NLO measurements.

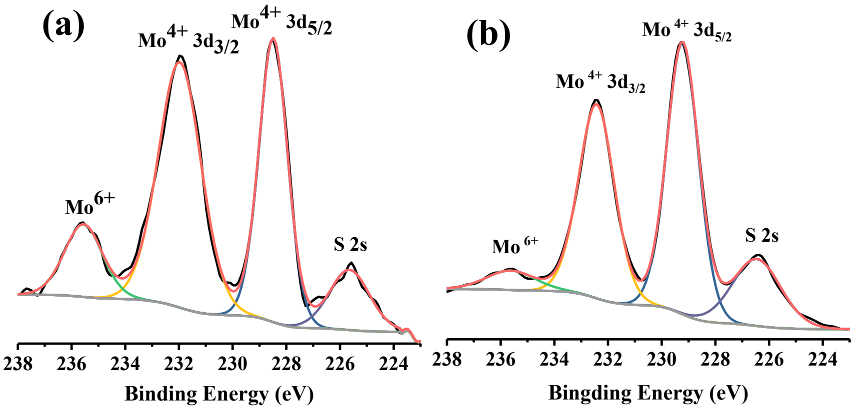


Figure S2. Mo 3d core-level XPS spectra of (a) MQDs and (b) MQDs-TPP.

As shown in **Figure S2**, the peaks at 232.0 and 228 eV in the high-resolution spectrum of Mo are assigned to Mo^{4+} $3d_{3/2}$ and Mo^{4+} $3d_{5/2}$, respectively. A small peak locating at 235.6 eV is ascribe to Mo^{6+}, which might be originated from the slight oxidation of Mo edges during the MoS_2 exfoliation and solvothermal process.[3] After react with porphyrin diazonium salts, Mo peaks are not significantly changed because the porphyrin molecules are only bonding with the S atoms at the top surface, and not with any Mo atoms in the middle of the S-Mo-S sandwich-like structure of MoS_2.[4]

Nonlinear Optical Properties of Samples

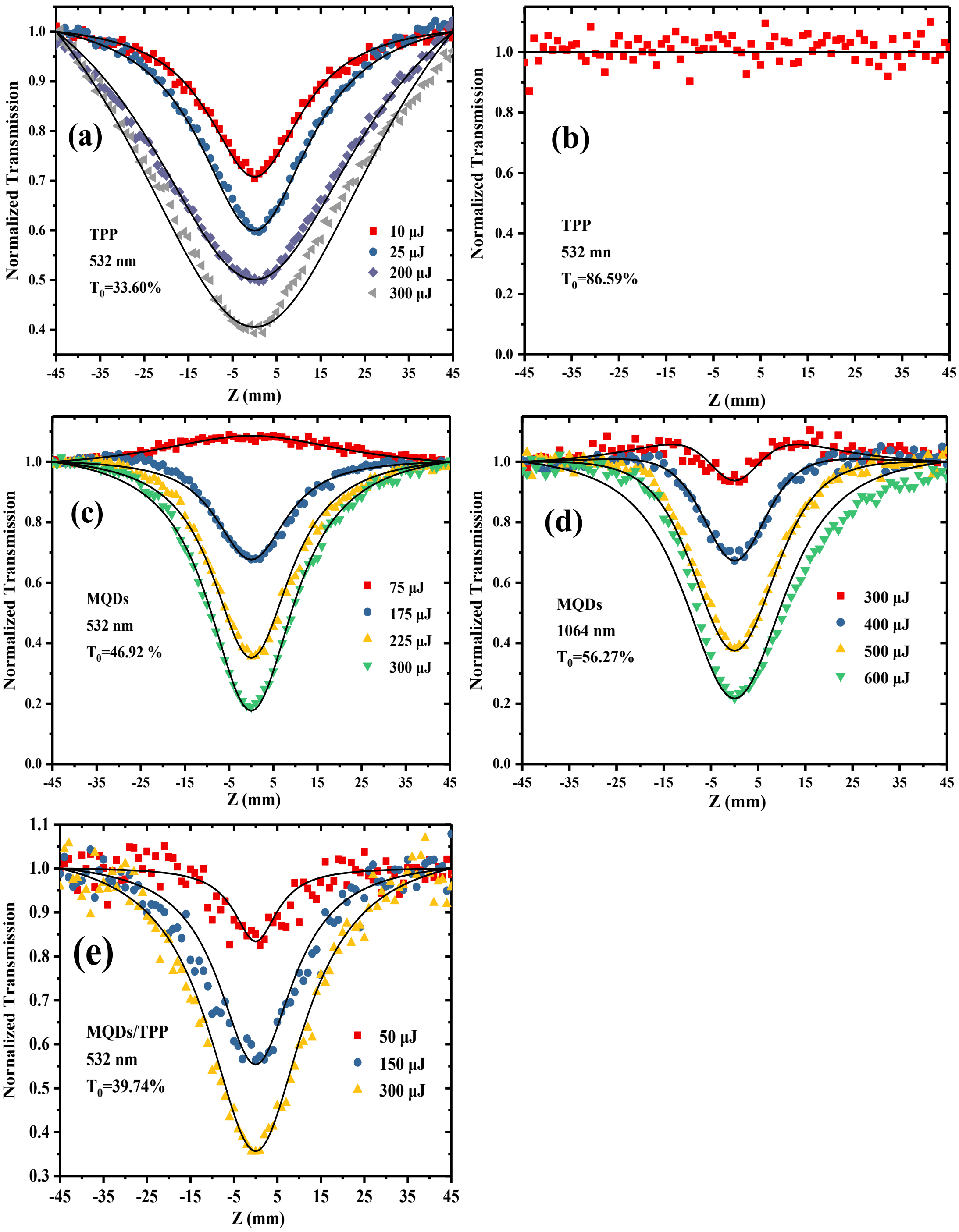


Figure S3. Typical open-aperture Z-scan data for PMMA-based films of samples excited under 6 ns pulses at (a, c, e) 532 nm and (b, d) 1064 nm. The solid lines are the theoretical fitting results.

For example, as shown in **Figure S3a**, all the intensity-dependent normalized transmittance (T_{min}) curves exhibited by the TPP/PMMA show symmetrical valleys with respect to the focus (z=0) at 532 nm, suggesting a typical RSA response, which usually arises in the material systems where the absorption cross section of ground state is much smaller than that of excited state. Furthermore, it can be observed for these films that the value of the valley transmittance at the beam focus decreases gradually with increasing input pulse energy at 532 nm. As expected, the TPP/PMMA film did not exhibit an NLO response at 1064 nm (**Figure S3b**). The MQDs/PMMA film shows saturable absorption (SA) at the low incident pulse laser energy of ~50 μJ due to the thermally induced nonlinear scattering (NLS) and RSA at higher pulse energy of >100 μJ at 532 nm. As shown in **Figure S3d,** The competitive process of SA and RSA also can be observed at low pulse energy regime (≤300 μJ). With the increase of pulse energy, the SA became negligible and the RSA became dominant, and as a result, the film showed good RSA behavior at high pulse energy regime. The NLO and OL performances of a control blend sample of TPP with MQDs (1: 1 weight ratio) was also investigated. As can be seen in **Figure S3e**, the achieved MQDs-TPP/PMMA film displays reverse saturable absorption (RSA) at the low incident pulse laser (50 μJ) intensity in which the T_{min} value decreases as the incident laser energy increases at 532 nm (0.82 at 50 μJ to 0.56 at 150 μJ to 0.36 at 300 μJ).

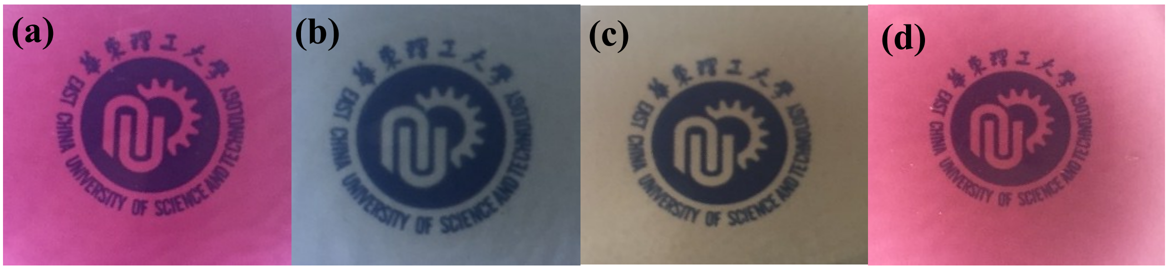


Figure S4. Digital pictures of (a) TPP/PMMA, (b) MQDs/PMMA, (c) MQDS-TPP/PMMA, (d) MQDs/TPP/PMMA thin films.

References

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