

Supporting information

Polymer Functionalized Antimony Sulfide Quantum Dots for Broadband Optical Limiting

Guangwei Li,^{b#} Qian Chen,^{a,b#} Ningning Dong,^{c,d} Haidong He,^{a*} Jun Wang,^{*c,d} Yu Chen^{*b}
^aMinhang Hospital, Fudan University, 170 Xinsong Road, Shanghai 201199, China. Email: chinahhd@sina.com

^bKey Laboratory for Advanced Materials, Institute of Applied Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China. Email: 3148704620@qq.com

^cPhotonic Integrated Circuits Center, Key Laboratory of Materials for High-Power Laser, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China. E-mail: jwang@siom.ac.cn

^dCenter of Materials Science and Optoelectronics, University of Chinese Academy of Sciences, Beijing 100049, China

These authors contributed equally.

Experimental Section

General : All reactions were carried out under dry nitrogen atmosphere by using standard Schlenk techniques. Organic solvents were purified, dried and distilled under dry nitrogen. The Sb₂S₃ quantum dots was prepared according to the literature.¹ Ultraviolet/visible (UV/Vis) absorption spectra were measured on a Shimadzu UV-2540 spectrophotometer. The TEM images were recorded on a JEOL JEM-2100 instrument. TGA was carried out on a Perkin–Elmer Pyris 1 thermogravimetric analyzer with a N₂ flow rate of 40 mL min⁻¹ at a heating rate of 10 °C min⁻¹. A HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer was used to record the steady-state fluorescence spectra. All samples for the fluorescence measurement were dissolved in water and/or dry organic solvent, filtered, transferred to a long quartz cell, and then capped and bubbled with dry nitrogen for 15 min.

The NLO and OL performances of the materials were investigated through a standard open-aperture Z-scan apparatus with 6 ns pulses from a Q-switched Nd:YAG laser at 1064 nm and its second harmonic at 532 nm. The laser beam was focused with a 15 cm lens. For the PMMA-based films, the repetition rate was set to 2 Hz.

Preparation of SQDs: In a typical procedure, 400 mg of Sb₂S₃ powder was added to 400 mL

of dry N-methyl-2-pyrrolidone (NMP), and then sonicated for 10 h in 30°C at the power of 250 W. The resultant dispersion was centrifuged for 30 min at speed of 8000 rpm. The supernatant containing SQDs was subjected to vacuum distillation to remove most of NMP, resulting in a black purple concentrated solution, which was then dialyzed in membranes with a molecular weight cut-off 3000 Da for three days. During dialysis, the deionized water was replaced with new one every 4 hours. The collected solution was freeze-dried for three days to give 50 mg of SQDs. This experiment was repeated for several times. Finally, ~200 mg of SQDs were obtained.

SQDs functionalized with mercaptoethanol (SQDs-ME). SQDs (100 mg) were added into 50 mL of DMF, and then were bath-sonicated for 40 min to give a well-dispersed solution. To the above solution was added 5 mL of mercaptoethanol under stirring, followed by heating at 130 °C for 24 h in the dark under nitrogen atmosphere. After removing the residual mercaptoethanol by vacuum distillation, the obtained SQDs-ME was re-dispersed into 40 mL of DMF.

Preparation of SQDs-DDAT. To the solution of SQDs -ME (40 mL) in DMF was added a mixture of DDAT (9.1 g) and *N, N'*-dimethylaminopyridine (DMAP, 1.84 g). After stirring at 0 °C for 1h, 1,3-dicyclohexylcarbodiimide (DCC, 5.19 g) was added to the above solution, followed by reaction for an additional 48h at room temperature. Then the reaction mixture was poured into 300 mL of methanol and vacuum-filtered through a polycarbonate film (ϕ 0.22 μ m). The collected product was washed with ethanol, deionized water and THF, respectively, to remove any adsorbed unreacted DDAT. 132 mg of SQDs -DDAT after dryness under vacuum at 40°C for 24h was obtained.

Preparation of SQDs-PVK . Polymerization reaction was carried out under highly purified dry nitrogen by use of standard Schlenk tube. A degassed mixture of SQDs-DDAT (100 mg) as RAFT agent, *N*-vinylcarbazole (NVC, 200 mg, before use, it was recrystallized twice from methanol at 40 °C, freeze-dried, and stored in vacuum in the dark), AIBN (4 mg) as initiator was heated in a water bath of 75 °C in a ultrasonic generator for 4 h under ultrasonic irradiation. After completion of the reaction, the mixture was allowed to cool to room temperature. The crude product was dissolved in DMF and dropped into 80 mL of methanol,

followed by a vacuum-filtering through a polycarbonate film ($\phi 0.22 \mu\text{m}$). The collected solid product was washed with a large amount of CH_2Cl_2 to remove any possible unreacted monomer and soluble free PVK polymer (if any) trapped in the resultant product. The product was further purified by Soxhlet extraction with acetone. After drying in vacuum at 50°C for 6 hours, 189 mg of SQDS-PVK was obtained.

Preparation of PVK: Polymerization reaction was carried out under highly purified dry nitrogen by the use of a standard Schlenk tube. A degassed mixture of DDAT (10 mg) as the RAFT agent, N-vinylcarazole (200 mg), and AIBN (3 mg) as the initiator was heated in a water bath of 75°C in a ultrasonic generator for 4 h under ultrasonic irradiation. After completion of the reaction, the mixture was allowed to cool to room temperature. The crude product was dissolved in CH_2Cl_2 and dropped into 120 mL of methanol. This process repeated for at least three times to remove any possible unreacted monomer and initiator. After drying in a vacuum at 50°C for 6 hours, 191mg of PVK powder was obtained.

Preparation of PMMA-based films : The sample (SQDs, SQDs-PVK, the SQDs:PVK blends) was added to a cyclohexanone solution of PMMA (100 g.L^{-1}) at a partial concentration $\sim 0.5 \text{ g.L}^{-1}$ for SQDs-PVK, and $\sim 1 \text{ g.L}^{-1}$ for both the SQDs and SQDs:PVK blends with a weight ratio of 1:1. This was followed by sonic agitation until a well-dispersed solution was formed. By using multilayer conventional spin casting technique^{1,2}, we achieved PMMA-based films which were further dried at 60°C for 24 h under high vacuum to remove any possible residual organic solvent before NLO measurements.

References

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