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Two-photon lithography in a porous polymer film

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1. General Information

All reagents and solvents are available commercially and used without further purification. Home-built devices and designed programs are used to test two-photon absorption and two-photon fluorescence. UV-Vis spectra were collected on an Agilent Cary 60 spectrometer. Fluorescence spectra were taken at room temperature on the Hitachi F7000. Attenuation reflectance Fourier transformation infrared spectra were recorded on a Nicolet Is50 spectrometer. Transmission electron microscopy (TEM) images were taken on JEOL 1400 operated at an electron acceleration voltage of 300kV. DLS measurements were performed with a Malvern Zetasizer Nano ZS (Malvern, Herrenberg, Germany). The lithographic pattern is characterized by ultra-high resolution laser confocal microscope (Leica SP8-STED 3X).

2. Preparation of porous polymer film

2-(2-Methoxyethoxy) ethyl 2-methyl-2-acrylate (3g, 16mmol), polyethylene glycol dimethacrylic acid (0.44g, 0.8mmol, Mn=550), dodecylbenzene Sodium sulfonate (SDS, 60mg) and 100ml of distilled water were mixed in a 250ml three-necked flask, ultrasonicated for 5 minutes, and degassed for 1 hour at 70°C with stirring of 300rpm. After deoxygenation, 44mg of potassium persulfate (KSP) was dissolved in 2ml of distilled water and slowly dripped into the reaction solution for overnight reaction. After the reaction was complete, the generated microgel was dialyzed (with a molecular weight cut-off of 8000-14000) for purification.

3.Uv-vis and Fluorescence of NTB without HIP

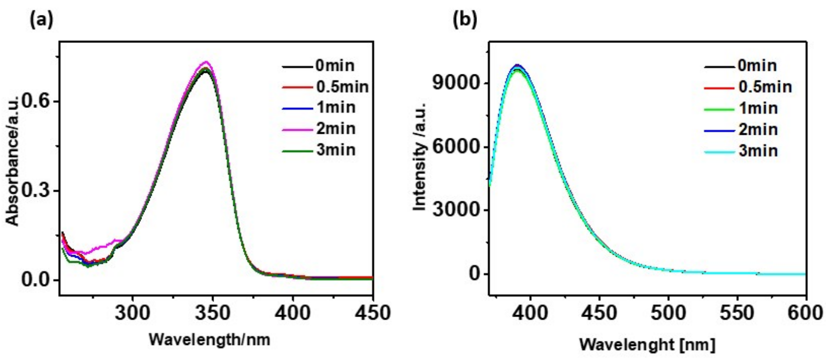

Fig. S1 a) steady-state photolysis of NTB in THF upon irradiation by the LED@365nm; UV-Vis spectra recorded at different exposure times; b) Fluorescence of NTB in tetrahydrofuran;
the solution of NTB without HIP would not show the decrease in UV-VIS and in FLS after photoirradiation

4. FT-IR spectra of precursor in the film upon exposure to 365 nm LED light at different time

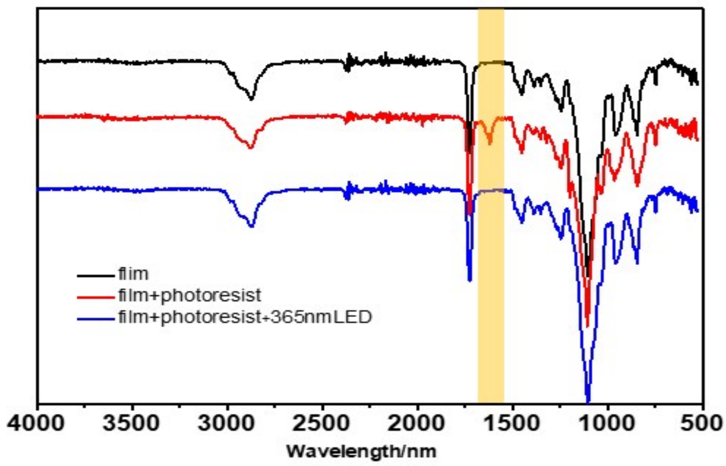

Fig. S2 FT-IR spectra of the NTB (0.1 wt.%)/HIP(1 wt.%)/TEGDVE mixture in the film upon exposure to 365 nm LED light at different time. The C=C stretching band of TEGDVE is highlighted.

5. optical setup of lithography

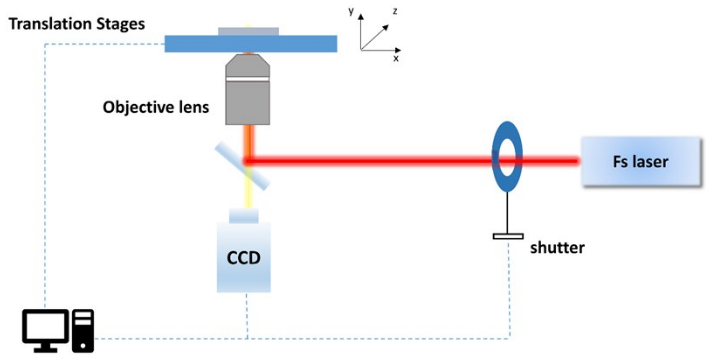

Fig. S3 The illustration of the optical setup.

6. Lithography programming

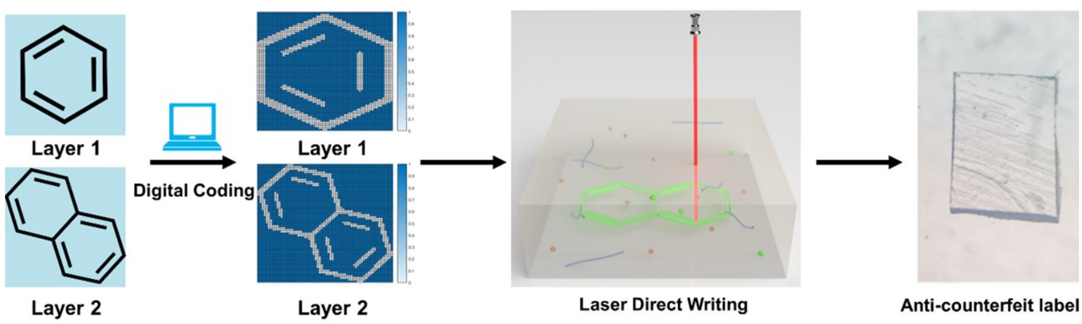

Fig. S4 Chart of lithography process.

7. Lithography in solution

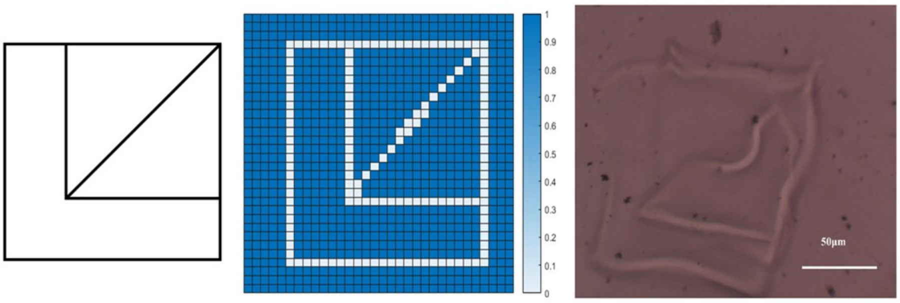

Fig. S5 Image of lithography in liquid.

8. single-photon lithography on polymer film

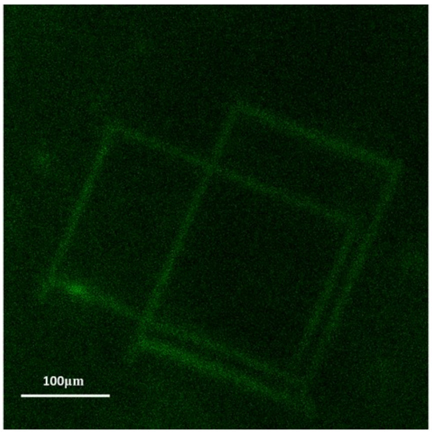

Fig. S6 single photon lithography. One layer is printed by focusing a CW laser (405 nm) on the surface of the film and another layer is printed by focusing the laser at 50μm below the surface, but the created two layers overlap in the z direction, which suggests poor printing resolution in the z direction by single photon lithography.