Supporting Information

**Super-resolution Interference Lithography Enabled by Non-Equilibrium Kinetics of Photochromic Monolayers**

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## Optical Setup for point-by-point writing

An in-house built stimulated emission depletion microscope was modified for direct laser serial writing in spirothiopyran resists. The schematic of our optical setup is shown in Figure S1. The microscope uses a Picoquant LDH DC 640 laser for excitation, MPB- PRFL-P-30-775 laser for depletion, custom Abberior galvanometer scanner, electronics and acquisition software, Olympus UPLSAPO100XO Objective lens and a SPCM-AQRH-13-FC Excilitas single photon counting module for detection of fluorescent photons. A vortex phase plate (RPC Photonics VPP-1c) is used to engineer a donut shaped intensity profile for the depletion beam.

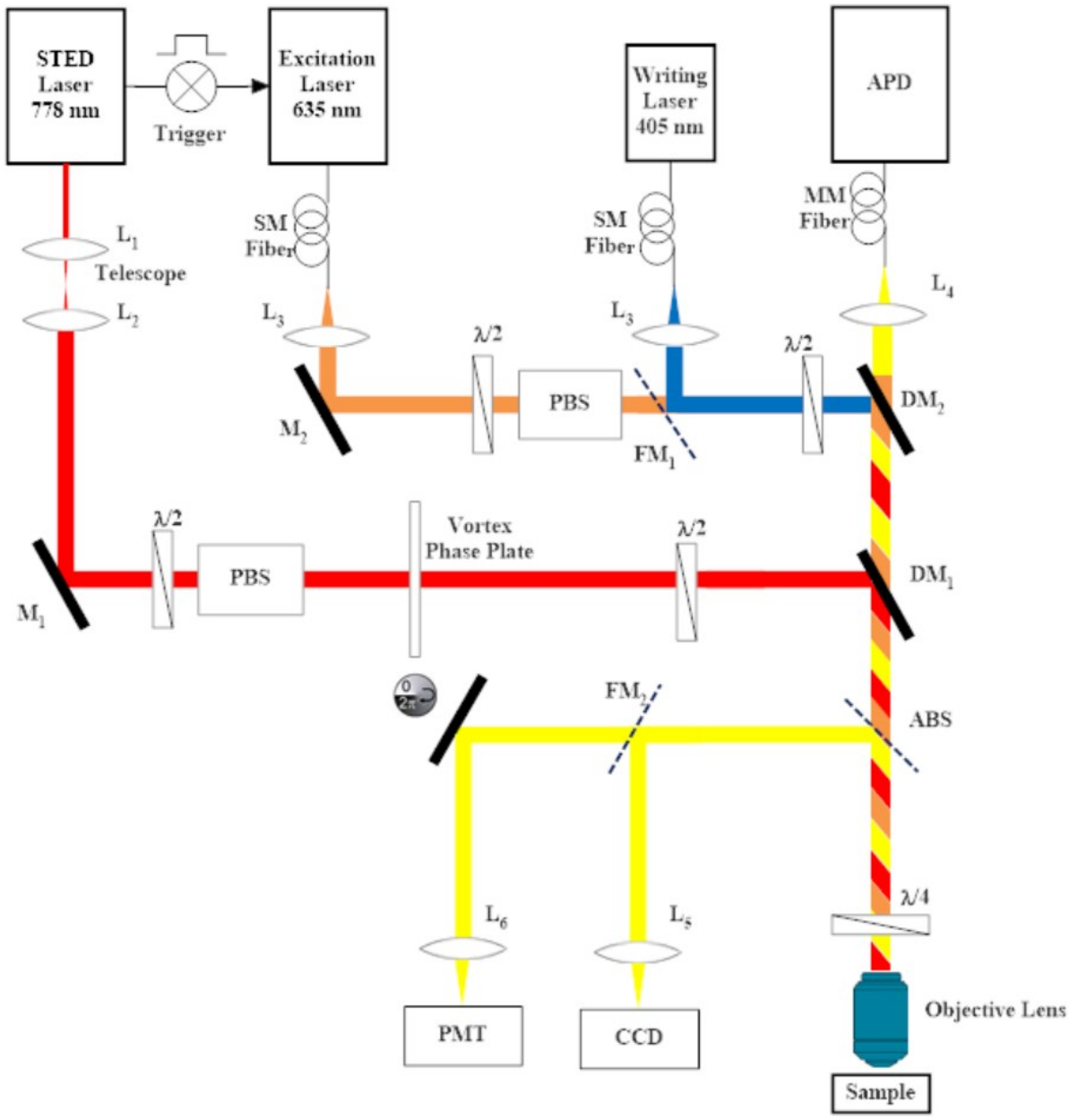


**Figure S1: Schematic of a modified custom stimulated emission depletion (STED microscope) used for focused direct writing using spirothiopyran resists. DM, FM, ABS, PBS designate the various dichroic mirrors, flip mirrors, auxiliary beam splitters and polarizing beam splitters used in the setup respectively. SM and MM stand for single and multi-mode fibers. λ/2 and λ/4 denote the half and quarter waveplates. PMT and CCD. The various lenses used in the setup are labelled as $L_{n,}$ , where n in an integer.**

A 405 nm laser (Power technologies, LDCU8/9189) is used as the light source for switching the spirothiopyran resist into the reactive merocyanine form. Light from this laser is collimated, after

outcoupling from a single mode fiber (Thorlabs P1-405B-FC-1) and added to the excitation laser beam-path using a flip mirror. The maxima of the point spread point spread function of the 405 nm beam is aligned precisely with the minima of the 778 nm beam by imaging gold beads (Nanopartz, A11-40-NPC-DIH-BULK) onto a photomultiplier tube detector (Thorlabs PMM02). Both lasers are operated at 40 MHz frequency. Writing is done by scanning the resultant beam configuration on the spirothiopyran functionalized coverslips,. The coverslips are exposed to a 0.8 μM Atto 647N Maleimide (Atto-Tec GmBH) in acetophenone. The intensity of the 405 and 778 nm beams at the back-focal plane of the objective lens was calculated to calculated to be 1.5 $mW/cm^2$ and 300 $mW/cm^2$ respectively. Lines are written at scan speed of 2 μm/s. After writing, the coverslips are washed with copious amounts of methanol, dried and loaded with thiodiethanol (TDE) for STED super-resolution imaging in the same setup. The 778 nm laser serves as the depletion light source for both super-resolution writing and imaging.

## Optical Setup for 2-color Interference Lithography

For parallel nanopatterning, we formulated a 2-color lithography scheme combining a 1D interference pattern created using a 532 nm CW diode pumped laser (Cobolt, Samba 532 05-01) in a Mach-Zehnder configuration and a plane wave of UV, generated using a collimated LED (Thorlabs M365LP1). A 2X telescope was used to magnify the beam emitted from the laser to 1.4 mm diameter. Care is taken to ensure that the polarization of the two incident green beams was kept parallel to the sample plane. A piezo mirror coupled to a fringe stabilizer (Odhner holographics Stabilock II) was used to correct for path length compensation and sample drift. The resulting optical setup is shown in Figure S2

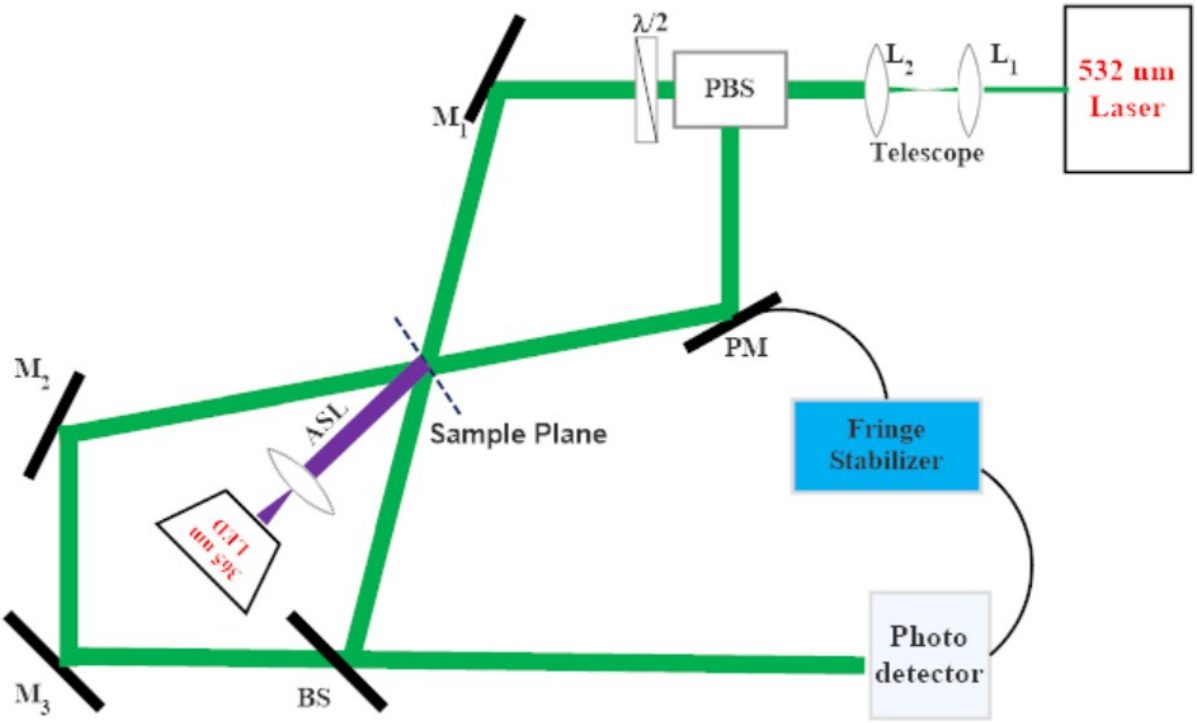


**Figure S2: Schematic of 2-color Interference lithography setup. PM, BS, PBS and AS stand for the piezo mirror, non-polarizing beam splitter, polarizing beam splitters and aspheric condenser lens used for UV LED collimation respectively. λ/2 denotes the half waveplates used to match the polarization between the two green arms. The various lenses and mirrors used in the setup are labelled as $L_n$ and $M_n$ respectively, where n in an integer.**

Samples were prepared by taking 50 µl of a 0.8µM solution of Atto-647N Maleimide in acetonitrile and dropcasting between a spirothiopyran functionalized coverslip and a microscope slide with a 125 µm spacer in between, (Grace Bio Labs GBL654002). This assembly was placed at the sample plane shown in Figure S2 using an appropriate holder (Thorlabs XYF1). After 200 seconds of exposure, the monolayer samples were washed in methanol for 10 minutes and after drying, mounted in 10 µl of a 97% TDE solution for STED imaging.

## STED inspired Super resolution Interference Lithography with Multiple Exposures

For any given exposure in STED inspired interference lithography using spirothiopyran, the Michael addition reaction proceeds selectively at the nodes of the depletion standing wave. In other regions, the molecule is restricted to its inactive SP isomer. The reversible photoswitching of these molecules can allow them to potentially participate in a second exposure, after phase shifting of the depletion beam (Figure S3)), allowing for the patterning of lines with both sub-diffraction feature size and resolution.

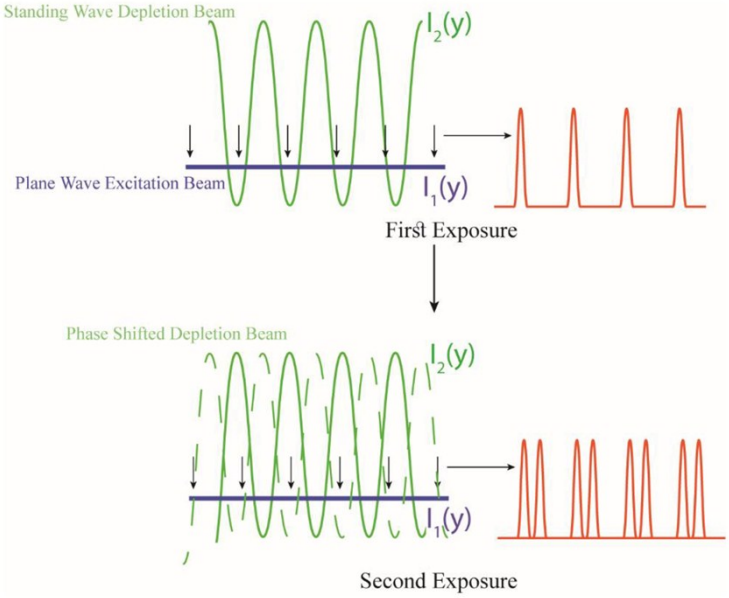


**Figure S3: Schematic illustrating how multiple exposures with a phase shifted depletion (green) beam could be used to fabricate lines with sub-diffraction spacing.**

The first exposure results in fluorescent lines being written at the node of the green standing wave. However, in our current sytsem, moving the position of the node of the standing wave during the second exposure was observed to erase the fluorescence from the first line. This is due to photobleaching of the covalently anchored dye under high green intensity.

As a proof-of-principle experiment to demonstrate that the molecules switched to the inactive spiro-isomer can be reactivated to participate in subsequent exposures, the sample orientation was rotated by 90 degrees between two successive exposures. The resulting pattern obtained in shown in Figure S4.

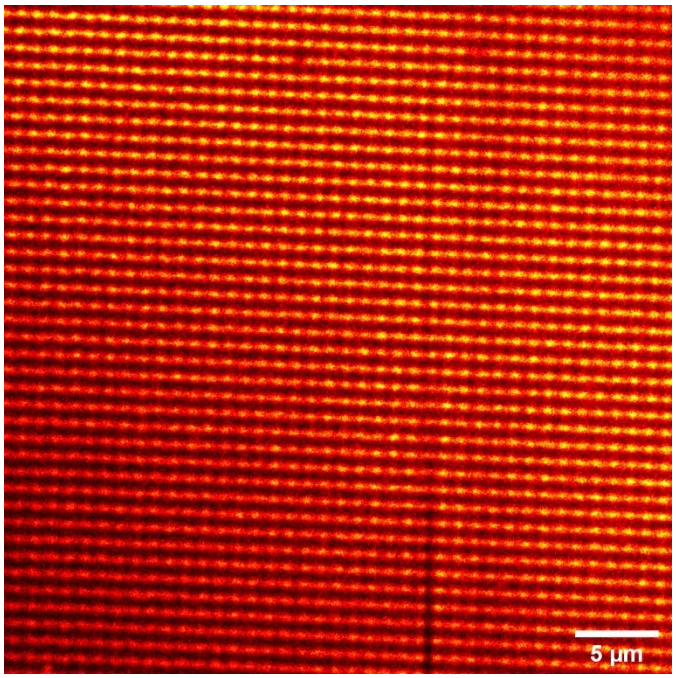


**Figure S4: Patterns obtained after two exposures on the spirothiopyran monolayer resist using super resolution interference lithography where the sample was rotated by 90 degrees between exposures.**

The horizontal lines were created in the second exposure. The weak contrast for the vertical lines in the nodes is ascribed to photobleaching of the lines written in the first exposure