Supplementary information

For

Two-photon photopolymerization directly initiated by spiropyran photochromic molecules

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1. Set-up for two-photon polymerization

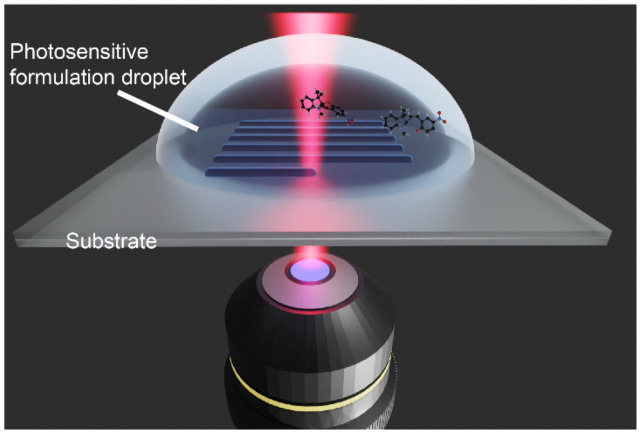

Figure S1 - Scheme showing the two-photon polymerization of a formulation composed of PETA monomer and Spy photochromes.

2. Absorbance measurements

Because the mixture of SPy in PETA leads under UV irradiation to photopolymerization, it is not suitable to use cuvettes to measure the absorption spectrum of such SPy solution dissolved in PETA. We tried to spin-coated the solutions on the glass substrate that can avoid polymerization because of the oxygen-filled environment preventing them from polymerization. In this way, we prove that the SPy keeps its photochromic ability in PETA solutions, shown in Figure S2. 50mg solution were dropped on a glass substrate and spin-coated at 2000 rpm during 30s.

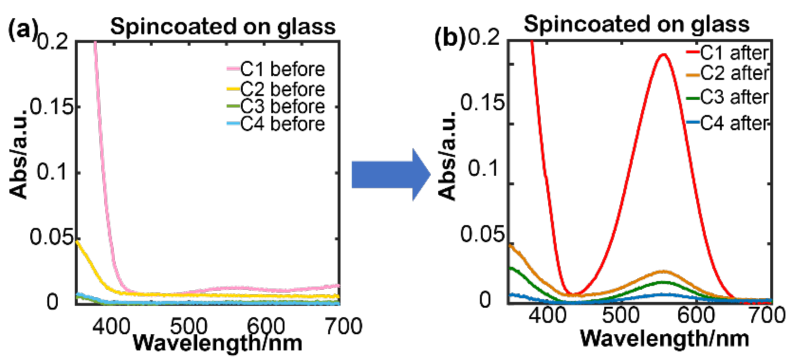

Figure S2 - Absorption spectra of the spin-coated samples of formulations with different concentrations of SPy dissolved in PETA, (a) before and (b) after UV irradiation of 10 min (C1 = 0.5 wt%, C2 = 0.05 wt%, C3 = 0.025 wt%, C4 = 0.0125 wt%).

3. Absorption spectra of Iragure 819, isopropylthioxanthone and 6nitro-BIPS in ethanol solution

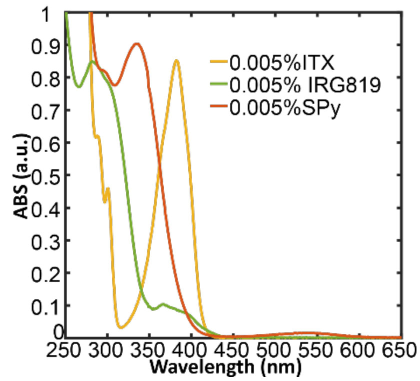

Figure S3 Absorption spectra of different photoinitiators (0.005 wt% in ethanol).

4. Measurement error of polymer linewidth

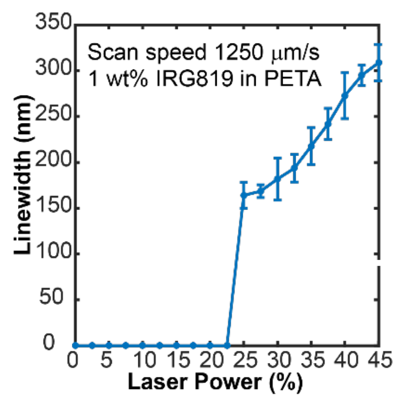

Figure S4 An example of the measurement error of polymer line width. The polymer lines are fabricated using 1 wt% IRG in PETA with a scan speed of 1250mm/s.

5. Reference experiment

We tried to fabricate polymer lines with PETA monomers (Fig. S5a) and a mixture between PETA and MDEA (Fig. S5b). According to these optical images, whatever the laser power or scan speed we used, these two formulations are unable to form shaped polymer lines as in Fig. 1e.

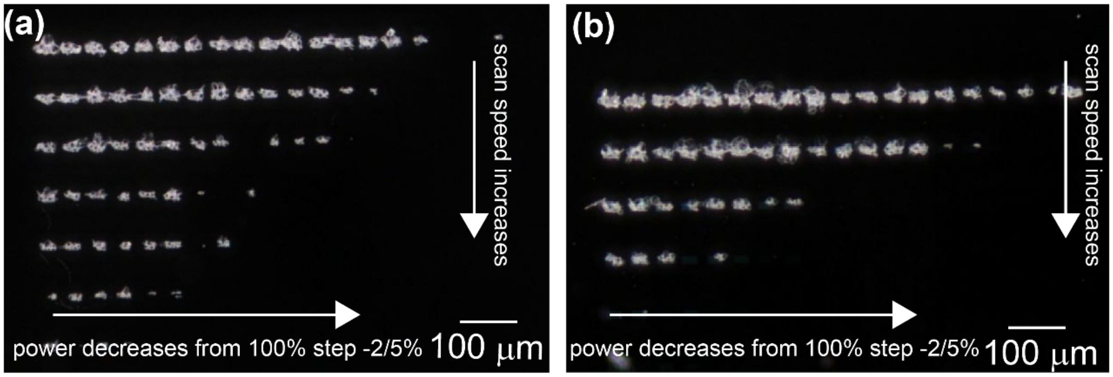

Figure S5 TPP attempt only using PETA monomer (a) and 15 wt% MDEA in PETA monomer (b).

6. MDEA influence

Fluorescence quenching is used to evaluate the influence of a molecule on another one. Specifically, if MDEA acts on the excited state of a type II photoinitiator, then the fluorescence of the latter should be quenched with an increased concentration of MDEA. As it cannot be performed directly in PETA because of polymerization issue, we used solvants in which MC presents the same absorbance spectrum than in PETA. For example, by comparing figure 7 and figure 6 of the manuscript, we can see that MC diluted in acetonitrile presents the same absorbance peak around 560 nm. The figure S6 (a) below shows the fluorescence spectra recorded with a solution of Spy (0.5%) in acetonitrile presenting different concentration of MDEA of 0.2 mol/L (3%w) and 0.5 mol/L (7.5%w). Each spectrum presents two peaks which is unusual for MC, normally only fluorescent at 640 nm. Moreover, the MDEA concentration seems to enhance the fluorescence at 640 nm and reduce the fluorescence at 560 nm. To understand this behavior, we performed absorbance spectra of these solutions presented in Figure S6 (b). We can observe that the MDEA increases the absorbance of the MC peak at low concentration and leads to the appearance of a shoulder on the blue side of the main absorption peak. This shoulder is known to come from the formation of MC dimeric species and/or monomer-solvent complex in the solution [1]. At this relatively high concentration of Spy (10^{-2} mol/L), this phenomenon is not unusual and we can conclude that MDEA seems to favor the formation of the MC isomer and thus the dimers at high concentration. The first fluorescence peak probably comes from new electronic states due to this aggregation. In acetonitrile, the influence of MDEA on the fluorescence spectra leads to think that SPy cannot be considered as a type II photoinitiator as the MDEA does not quench the MC fluorescence. However, in PETA, MDEA does improve the reactivity of SPy and we can conclude that it is probably due to the fact that it increases the concentration of the active isomer (MC) in the formulation.

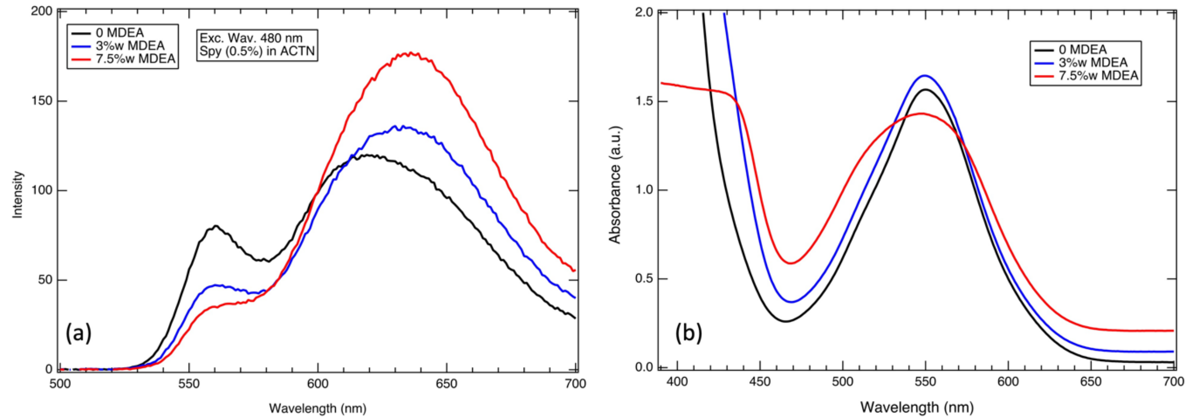

Figure S6: Influence of the MDEA on the SPy fluorescence (a) and absorbance (b) spectra

7. One-Photon-Photopolymerization kinetics

We performed IR spectroscopy to investigate the photopolymerization kinetics for SPy in PETA with and without MDEA, by following the absorption of the PETA C=C bond at 810 cm^{-1}.

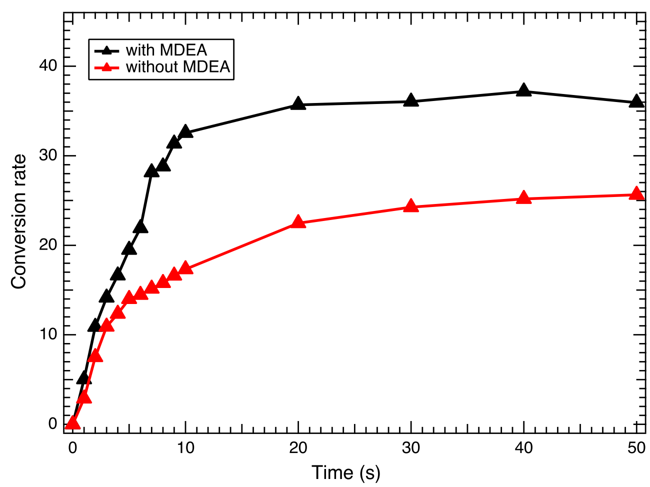

Figure S7: One-Photon photopolymerization kinetics recorded with solutions of SPy (0.5%) diluted in PETA with MDEA 5% (black curve) and without MDEA (red curve). The excitation wavelength is 385 nm.

8. Solvatochromism of 8 MeO-BIPS, 6 nitro 8 MeO-BIPS, 6 nitro-BIPS and SPOX

Solvent dependence experiments were performed to check the solvatochromism of all SPys' and the SPOX. For that purpose we used ethanol (polar) and dioxan (apolar) solvents. The absorption spectra of MC were obtained after 1mn UV irradiation at 365 nm. 8MeO-BIPS and SPOX spectra show a bathochromic (red) shift with increasing solvent polarity while 6nitro8MeO-BIPS and 6 nitro-BIPS spectra show a reverse behavior (blue shift).

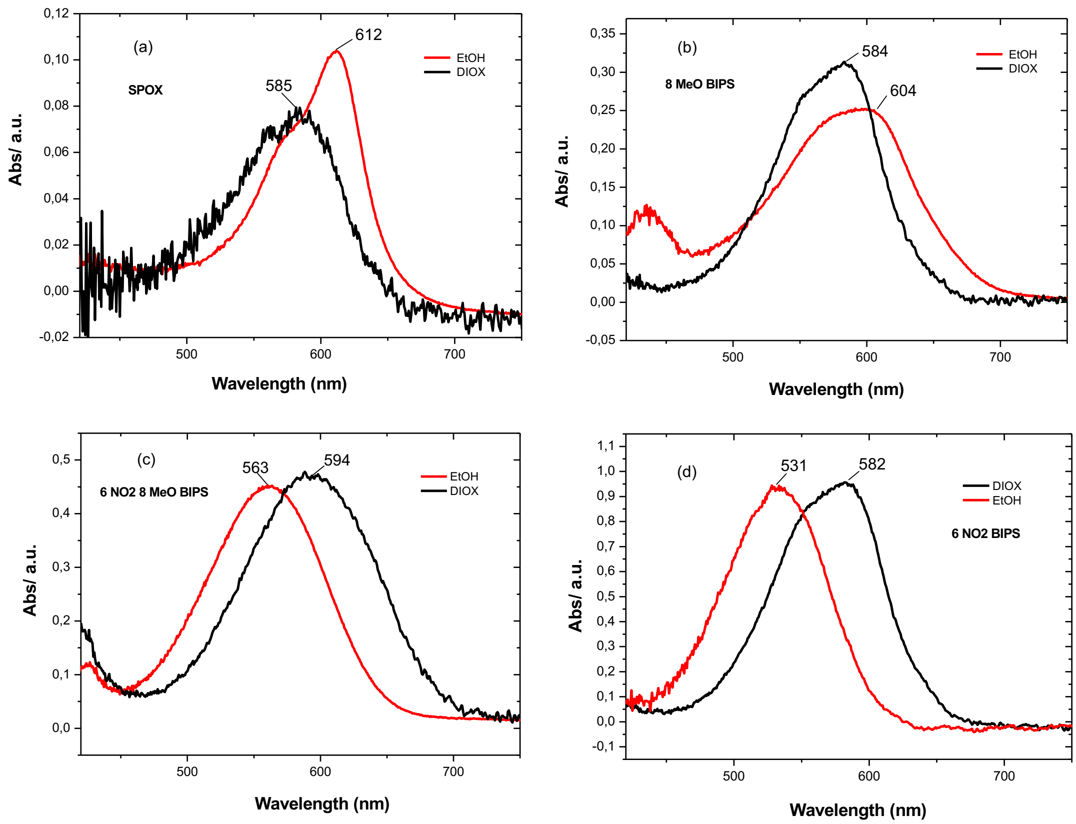

Figure S8 Absorption spectra of selected photochromes, obtained after UV irradiation at 365 nm, in Ethanol and Dioxan: (a) SPOX, (b) 8 MeO BIPS, (c) 6 NO2 8 MeO BIPS, (d) 6 NO2 BIPS

9. Two-photon polymerization attempts using *8MeO-BIPS, SPOX, 6nitro8MeO-BIPS and NAP*

1) 8-MeO-BIPS

We tried to use the PETA solution containing 1 wt% 8-MeO-BIPS to fabricate polymer lines with the use of Nanoscribe. And the results are shown in Figure S9, there are no formed polymer lines. Neither the formulation containing BIPS alone nor the other one with MDEA was able to successfully produce polymer lines. According to this, we can conclude that the 8-MeO-BIPS can't initiate TPP polymerization, it can't work as photoinitiator.

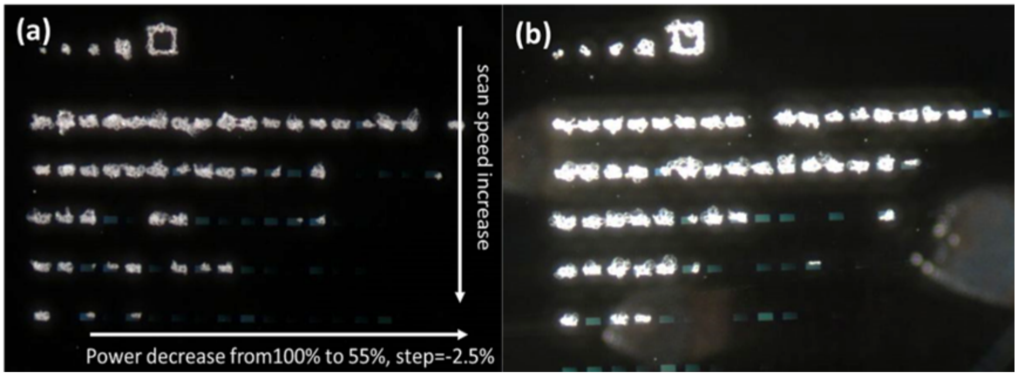

Figure S9 TPP attempt using (a)1% wt -8MeO-BIPS in PETA; (b) 1% wt 8-MeO-BIPS +10 %wt MDEA in PETA.

2) SPOX

As we did for SPy, we studied the TPP initiated by (SPOX). Figure S10 shows the dark-field image of the fabricated polymer lines using laser power from 100% to 55% (horizontal variation) and the scan speed changes from 100 μm/s to 2000 μm/s (vertical variation). For Figure S10 (a) we used a formulation of 0.5 wt% SPOX in PETA and for Figure S10 (b), the formulation was 0.5 wt% SPOX + 15 wt% MDEA in PETA. Regarding the results, SPOX can initiate TPP without any other initiators, and cooperating with MDEA does not increase the polymerization efficiency. Compared to the results obtained with a formulation of 0.5 wt% SPy in PETA, which can fabricate polymer lines using laser power below 45% with 500 μm/s scan speed, the 0.5 wt% SPOX needs power around 77.5% at the same scan speed. Hence, the efficiency of SPOX to initiate two-photon polymerization is much lower than that of SPy, and it doesn't have similar behavior as SPy or ITX after adding MDEA.

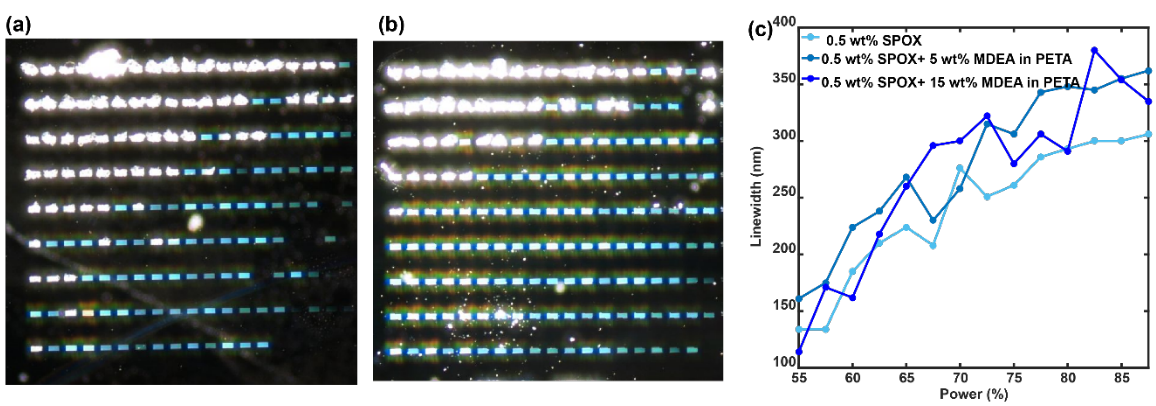

Figure S10 - TPP attempt using 0.5%wt SPOX in PETA (a) and (b) 0.5 wt% SPOX + 15 wt% MDEA in PETA. From top to bottom, scanspeed increases from 100 µm/s to 2000 µm/s and from left to right, laser power decrease from 100% by a step of 2.5%. (c) The polymer linewidths of the fabricated polymer line shown in (a) and (b).

3) 6-nitro-8-MeO-BIPS

TPP initiated by 6nitro8MeO-BIPS has also been attempted. Figure S11 shows the results. We compared a formulation of 0.5 wt% 6nitro8MeO-BIPS in PETA (Fig. S11 (a)) and the same formulation adding 10 wt% MDEA (Fig. S11 (b)). From the darkfield images recorded on the fabricated lines, 6-nitro-8-MeO-BIPS can initiate TPP without any other initiators and cooperating with MDEA increases the polymerization efficiency. As 0.5 wt% SPy in PETA can produce polymer lines using a laser power below 45% with 500 μm/s scan speed, whereas 0.5 wt% 6-nitro-8-MeO-BIPS just needs a power around 22.5% at the same scan speed, this indicates that 6-nitro-8-MeO-BIPS is more efficient to initiate 2PP. Besides, 6nitro8MeO-BIPS also present the same behavior as type II initiator.

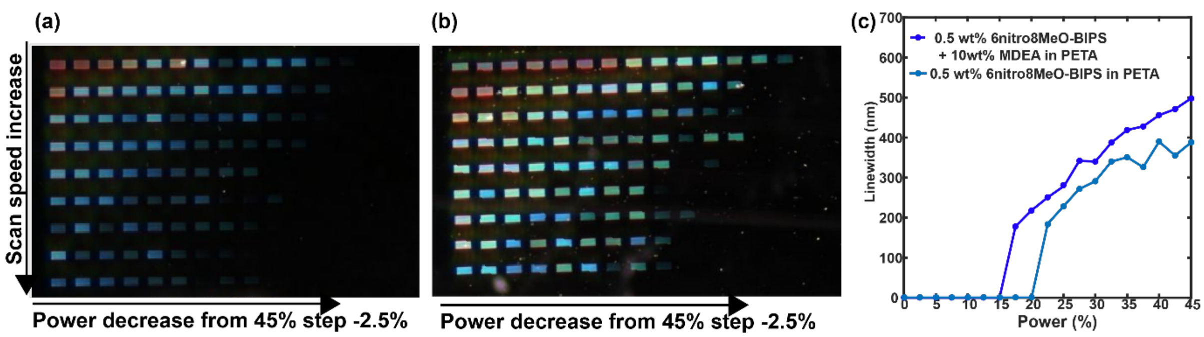

Figure S11 - TPP attempt using 0.5%wt 6nitro8MeO-BIPS in PETA (a) and (b) 0.5 wt% 6-nitro-8-MeO-BIPS+10 wt% MDEA in PETA. (c) The polymer linewidths fabricated using a scan speed at 500 μm/s.

4) NAP

According to Figure S12, although using the formulation of 0.5 wt% NAP in PETA or 0.5 wt% NAP+ 10 wt% MDEA in PETA allows to print some polymer lines, the resulted polymer lines weren't recognizable. Compared to the results in Figure S10, using 0.5 wt% NAP is even worse than using 0.5 wt% SPOX for TPP printing.

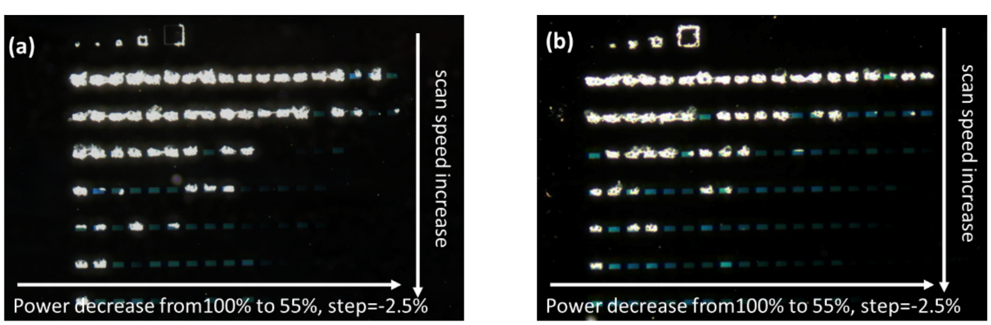

Figure S12 - TPP attempt using 0.5%wt NAP in PETA (a) and (b) 0.5 wt% NAP +10 wt% MDEA in PETA

10. References

[1] Flannery, J. B. Jr., The Photo- and Thermochromic Transients from Substituted 1’,3’,3'-Trimethylindolinobenzospiropyrans, Contribution from the Research Laboratories, Xerox Corporation, Rochester, New York 14603, 1967.