Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Geometry-driven Mass Transport Dynamics within Permeable 3D-Microstructures fabricated by Two-Photon Polymerization.

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images of the polymer dot recorded in ACN at the initial and final incubation time. Formulation: **PEGDA** mixed with **AMS** (7 mM) and **MDEA** (25 mM).

Figure S8. Evolution of the fluorescence signals from the excitation of two-photon patterned structures (20 x 20 µm square planes) during their incubation in ACN. The fluorescence images of each microstructure were recorded *in situ* before and after the kinetics. **A.** Microstructure based on formulation with **AMS** (7 mM) and **MDEA** (25 mM) ($\lambda_{exc.}$ = 365 nm). **B.** Microstructure based on formulation with **Rhodamine B** (8 mM) and **MDEA** (25 mM) ($\lambda_{exc.}$ = 485 nm). Inset: Fluorescence spectrum of the surrounding solvent recorded after the incubation of the microstructure with **Rhodamine B**. All structures were two-photon patterned at λ_{ex}: 780 nm (P = 15 mW, τ_{exp} = 2 ms).

Figure S9. AFM images of a dried two-photon polymerized square plane with 50 µm side. The fluorescence of the microstructure has been initially quenched upon incubation in an ACN solution of copper (II) cations (10^{-4} M). **A.** AFM topographic image. **B.** AFM height image.

Figure S10. Fluorescence quenching kinetics recorded at different X/L_{MAX} coordinates for each µm-structure. Insets: Initial fluorescence image with the *x*-axis referential and master 3D-image of the corresponding µm-structure.

Scheme S1. **A.** Scheme of the PTFE chamber. **B.** Time-dependent fluorescence intensity changes relative to three similar squares planes with a thickness of 1.75 µm.

Scheme S2. Molecular structures of the acrylate-based monomers.

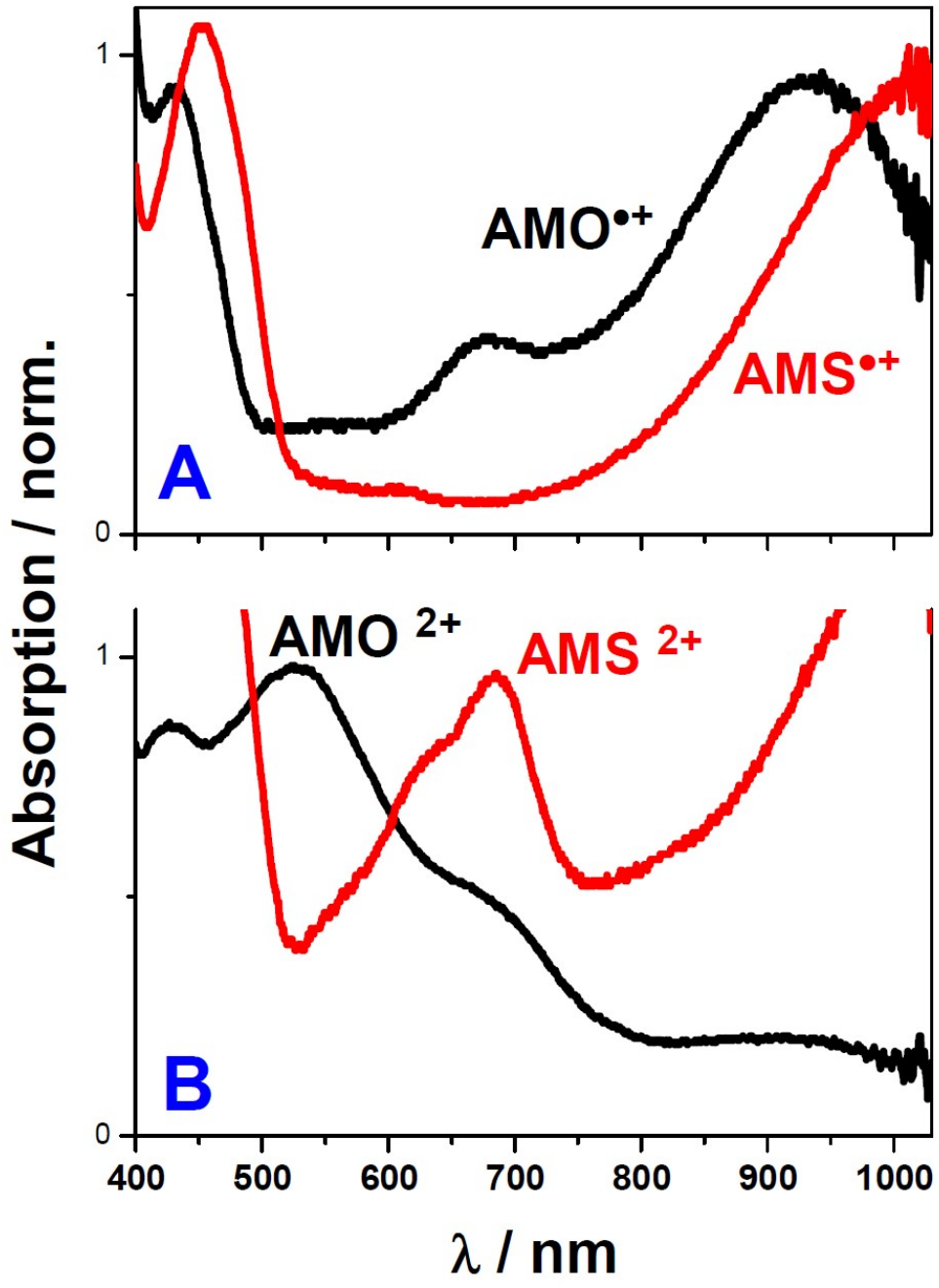


Figure S1. Comparison of the normalized spectroelectrochemical spectra of (**A**) radical cations and (**B**) dications of **AMO** and **AMS** in ACN + $(nBu)_4NPF_6$ (0.1 M)

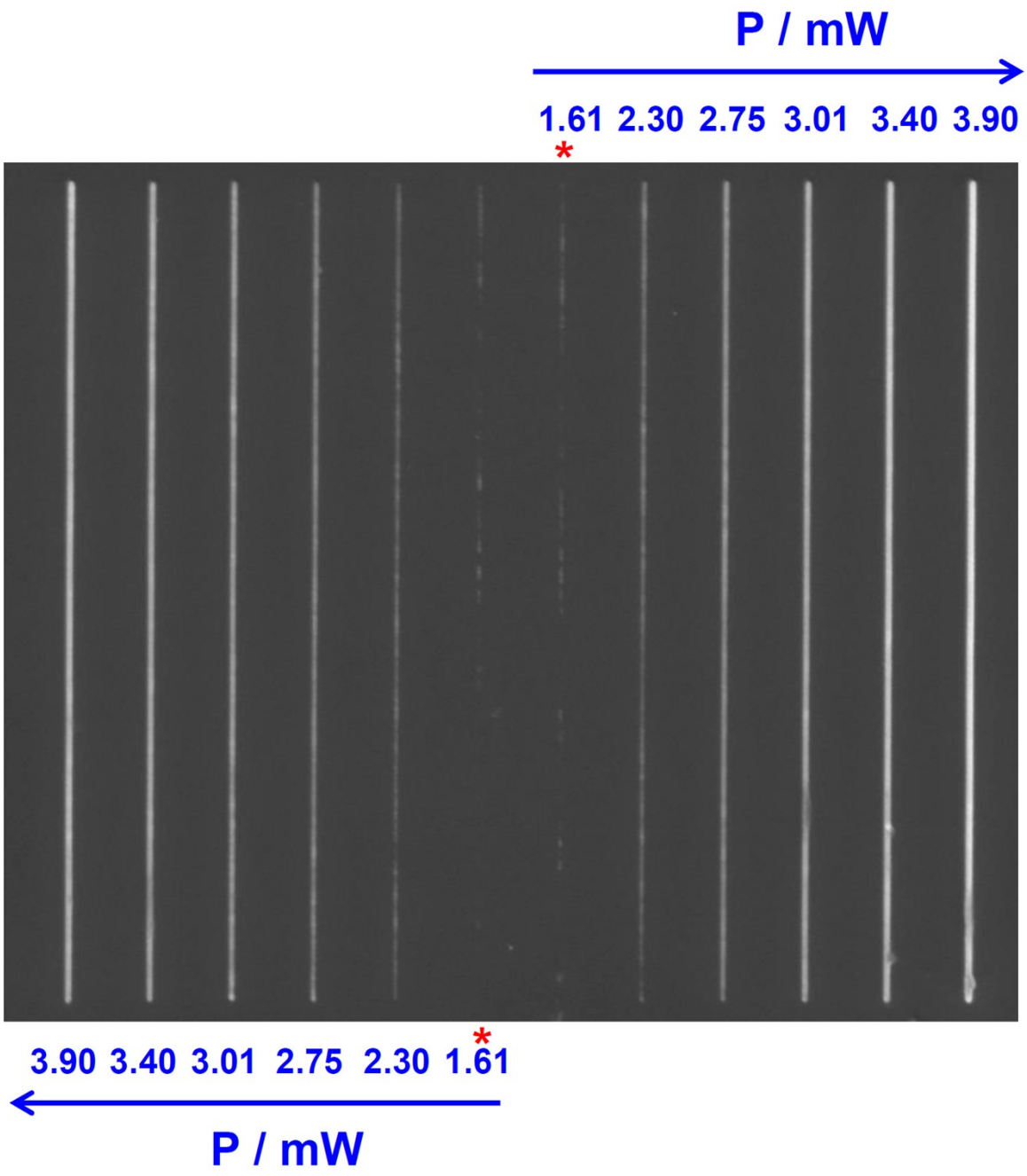


Figure S2. SEM micrograph of symmetrical 2P induced polymerized lines fabricated for distinctive laser excitation powers (λ_{ex} = 780 nm, τ_{exp} = 10 ms). The star pictogram indicates the corresponding value of P_{th} at 780 nm. Formulation: Triacrylate resin (**PETIA**) mixed with **AMS** (7 mM) and **MDEA** (25 mM).

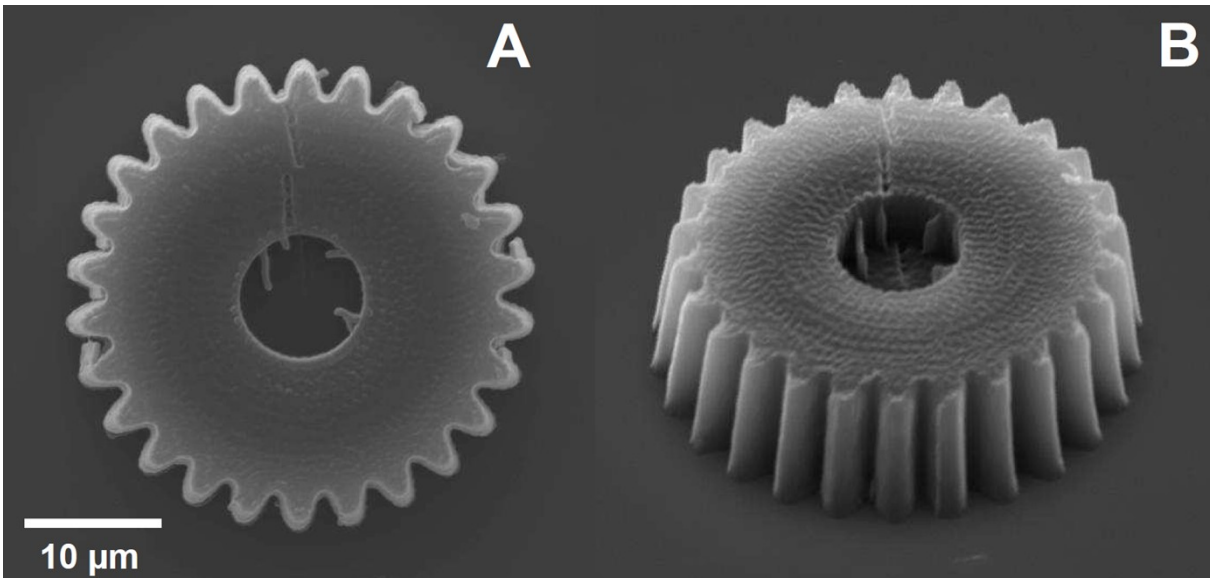


Figure S3. SEM images of a 2PP fabricated microgear (**A** : front view, **B** : view tilted at 45 °). Formulation : **PETIA** with **AMS** / **MDEA** : 7 mM / 25 mM (λ_{ex} : 780 nm, P = 5 mW, τ_{exp} = 2 ms).

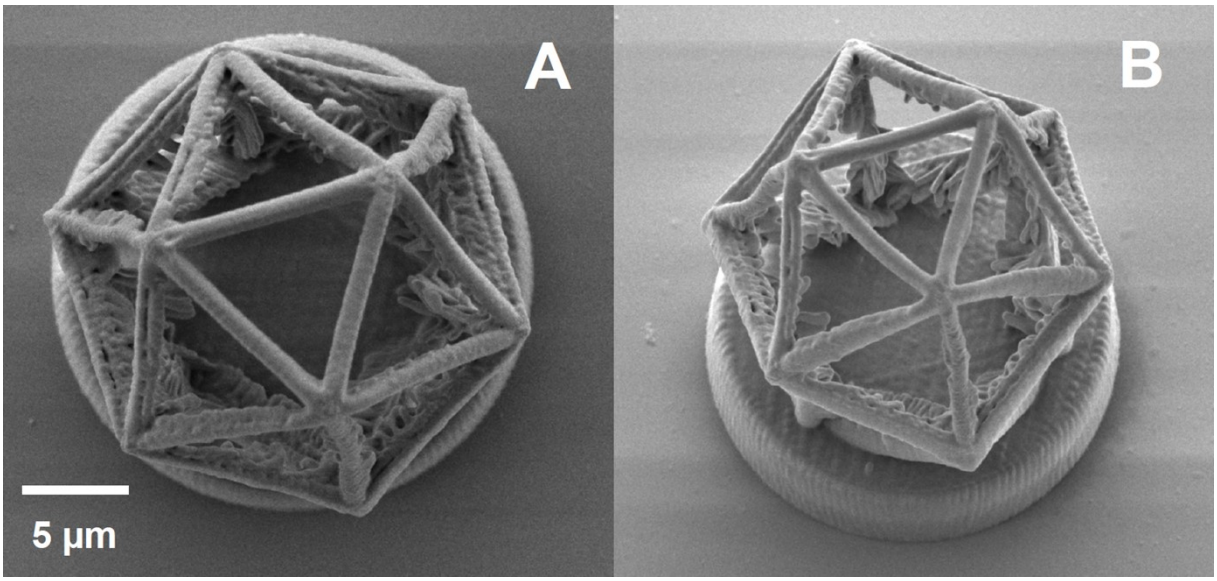


Figure S4. SEM images of a hollow icosahedral microstructure (**A** : front view, **B** : view tilted at 15 °). Formulation : **PETIA** with **AMS** / **MDEA** : 7 mM / 25 mM (λ_{ex} : 780 nm, P = 4 mW, τ_{exp} = 2 ms).

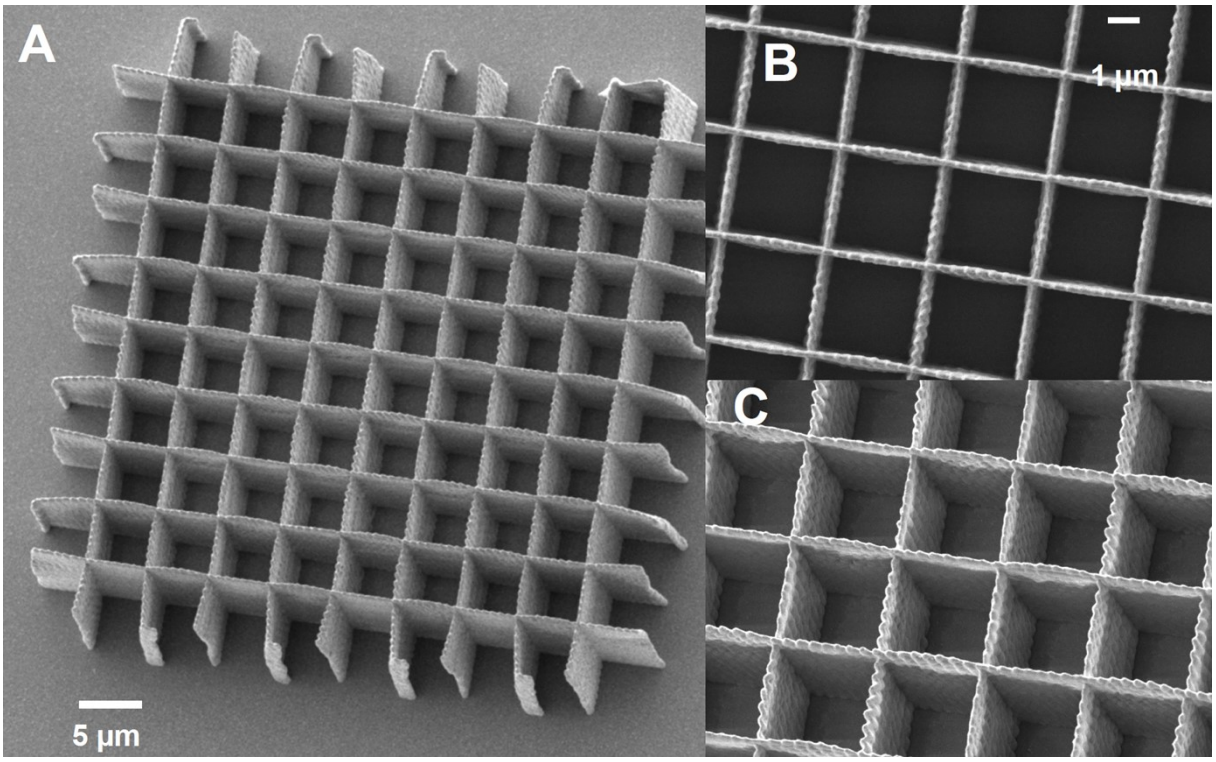


Figure S5. SEM images of a waffle-like microstructure (**A-C** : view tilted at 15 ° **B :** front view). Formulation : **PETIA** with **AMS** / **MDEA** : 7 mM / 25 mM (λ_{ex} : 780 nm, P = 4 mW, τ_{exp} = 2 ms).

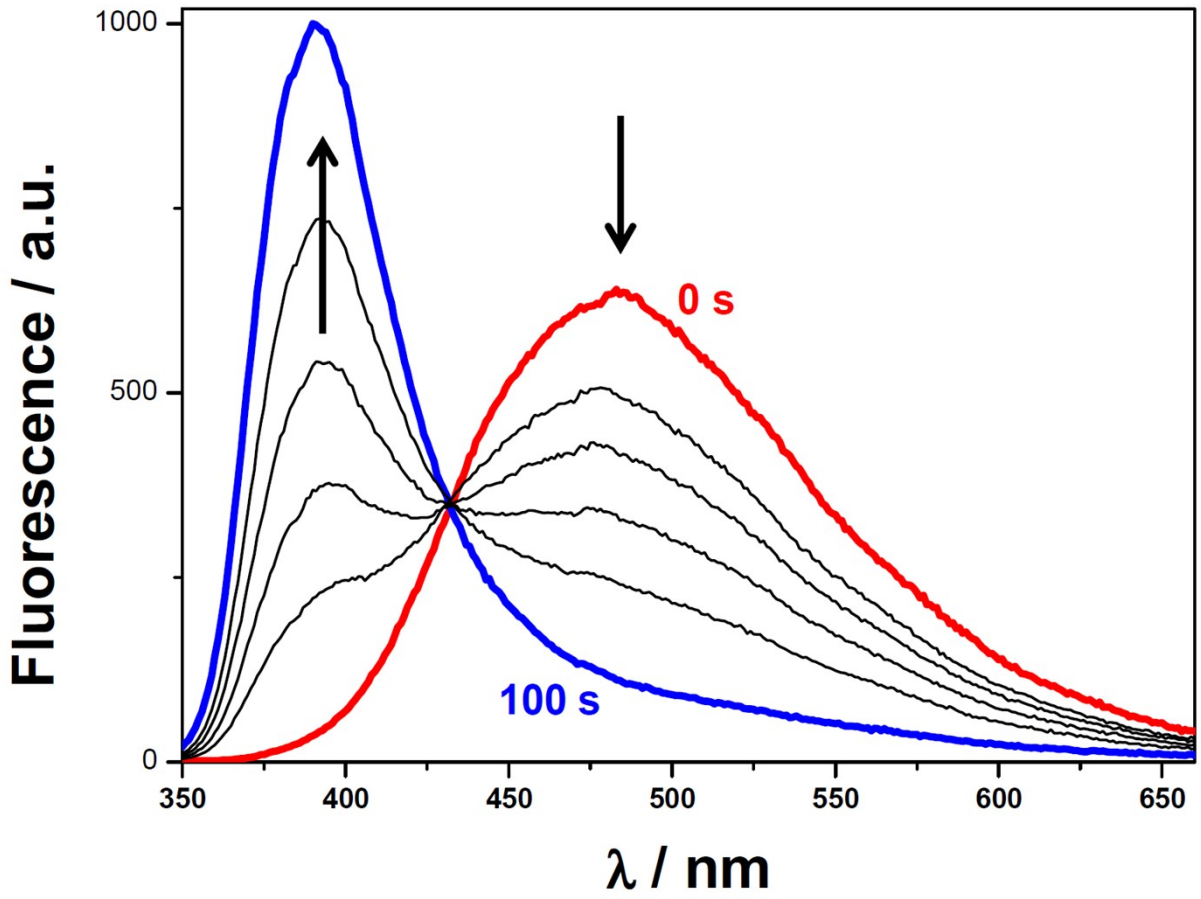


Figure S6. Evolution of the fluorescence spectrum of **AMS** in the triacrylate formulation upon stepwise photopolymerization at 365 nm. Formulation: Triacrylate resin (**PETIA**) mixed with **AMS** (7 mM) and **MDEA** (25 mM). Each fluorescence spectrum was recorded at $\lambda_{exc.}$ = 340 nm.

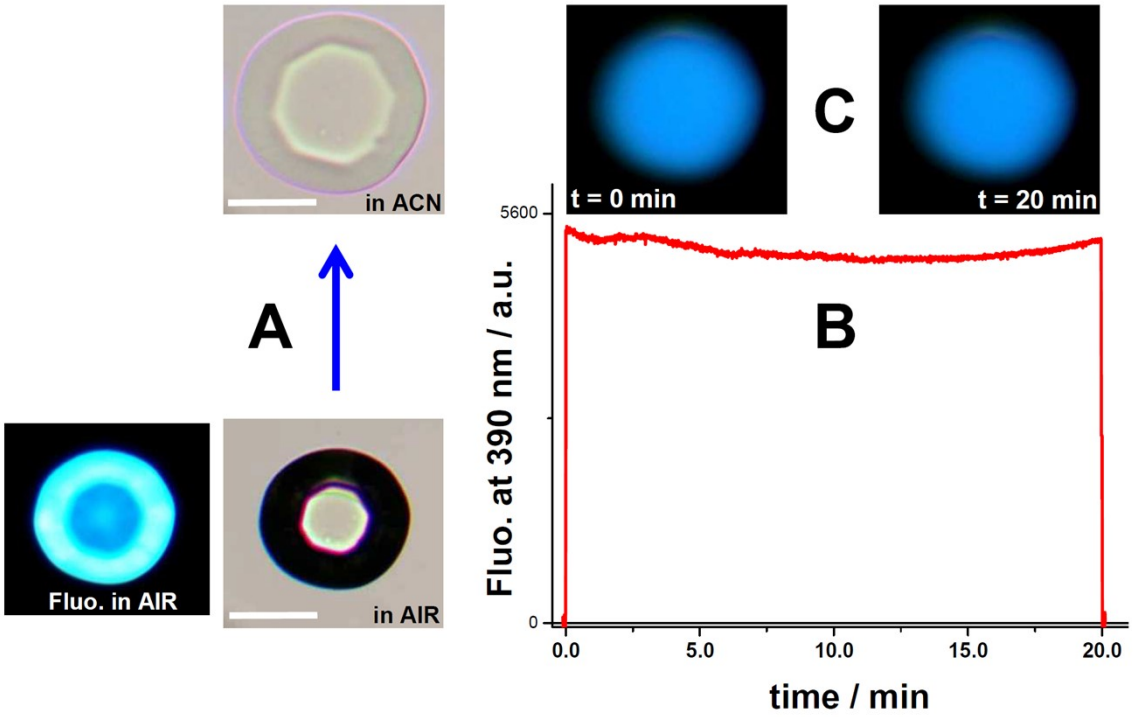
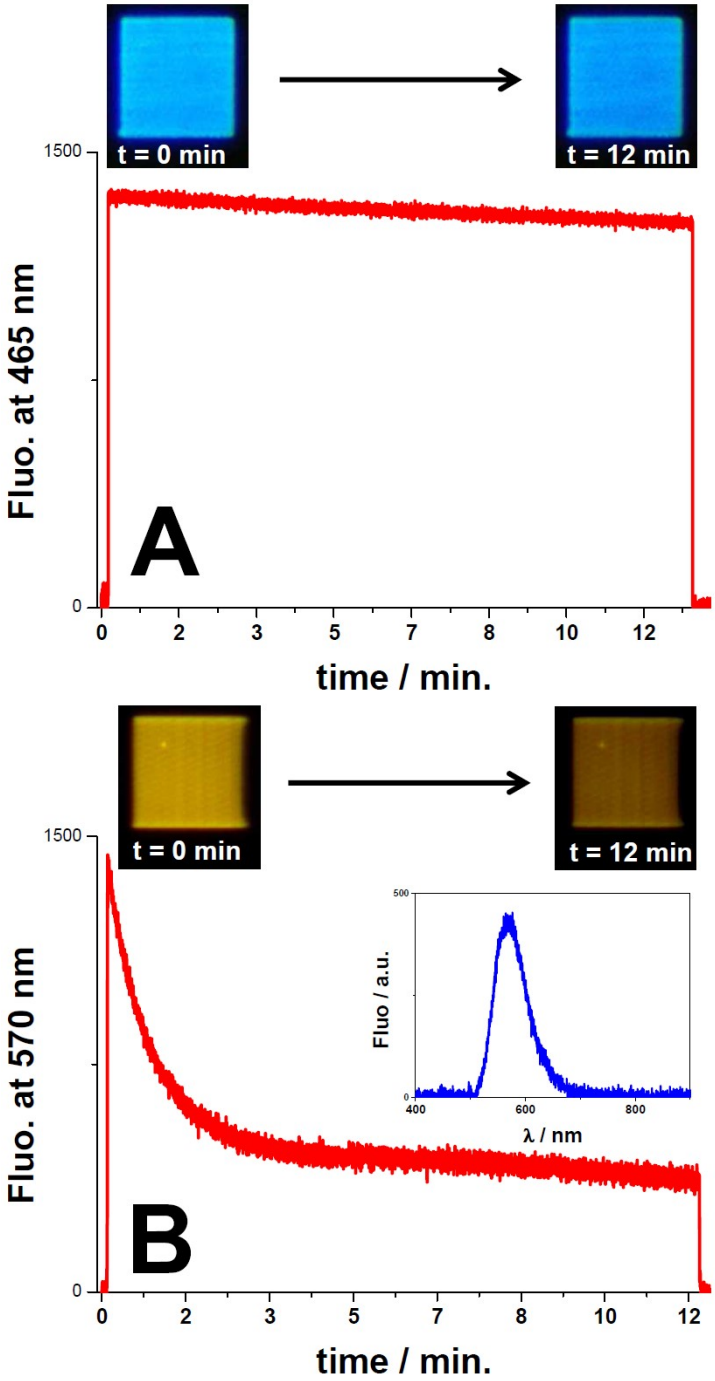


Figure S7. **A.** Transmitted optical images of a photopolymerized **PEGDA** dot in air and in ACN solution (scale bar: 40 µm). **B.** Evolution of the fluorescence signal recorded from the excited polymer dot during its incubation in ACN ($\lambda_{exc.}$ = 365 nm). **C.** Fluorescence images of the polymer dot recorded in ACN at the initial and final incubation time. Formulation: **PEGDA** mixed with **AMS** (7 mM) and **MDEA** (25 mM).



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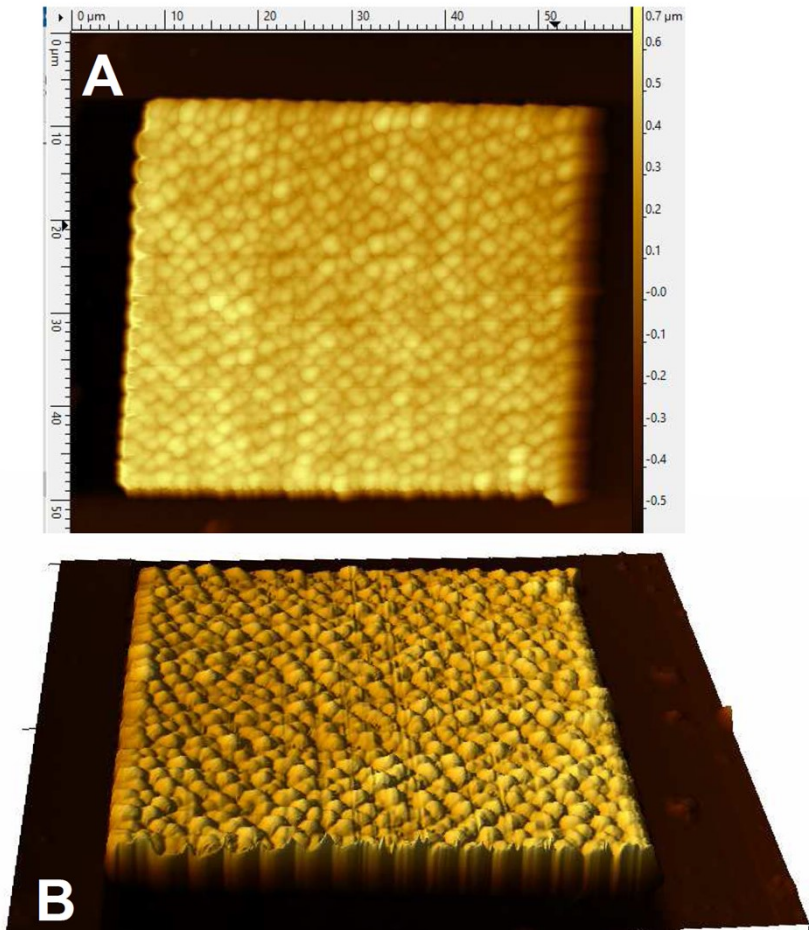

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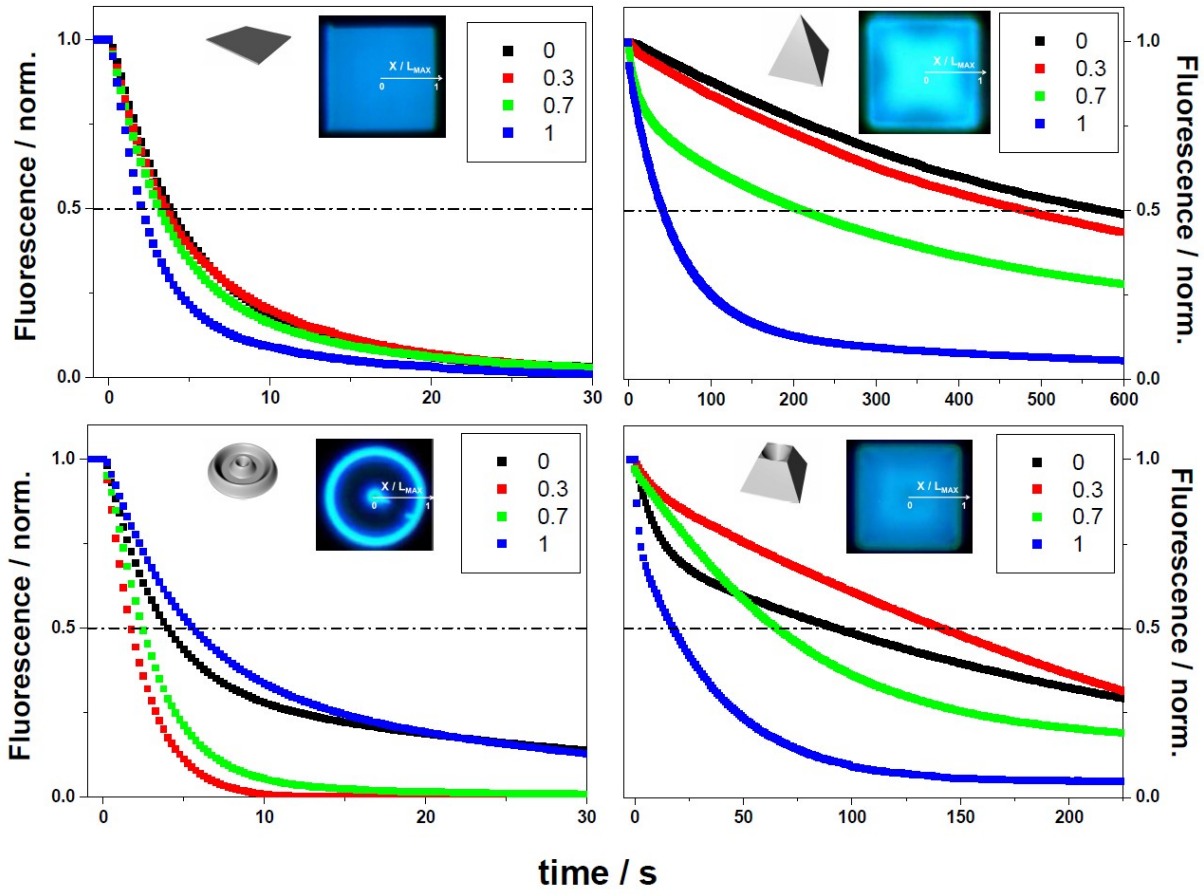

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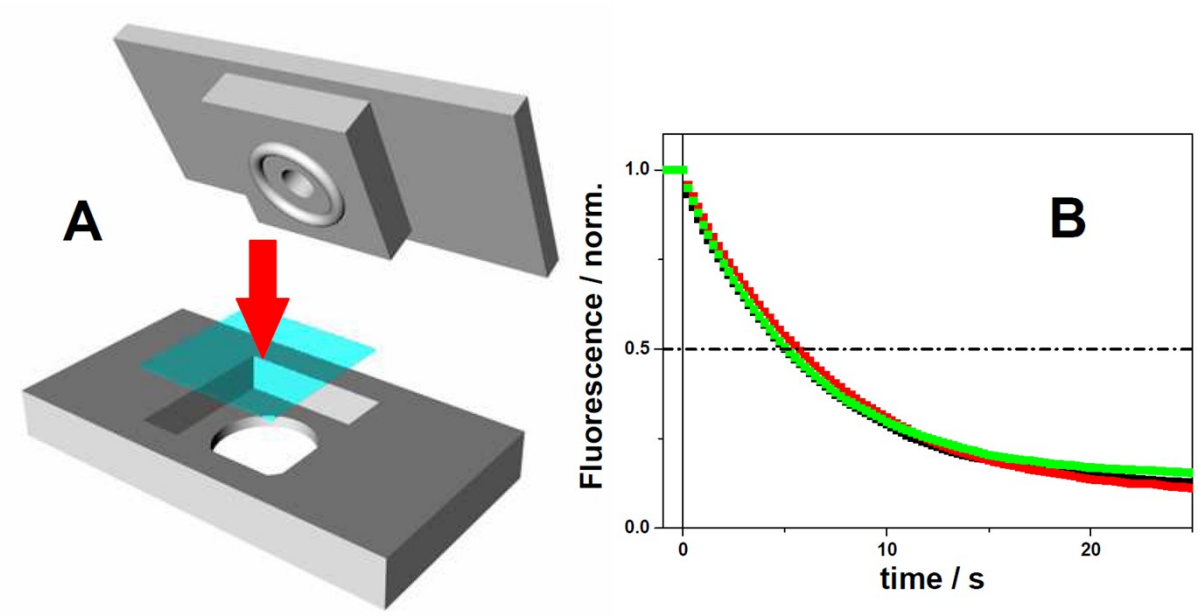

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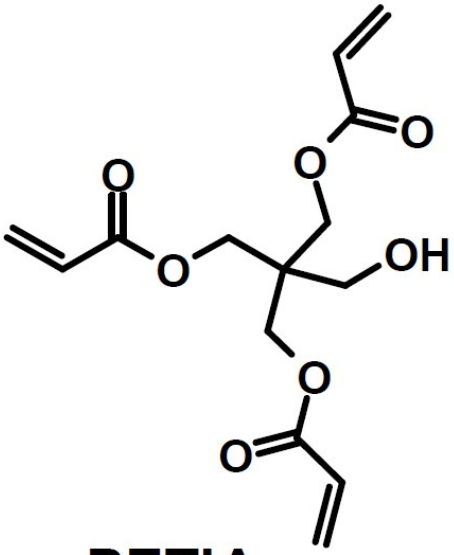
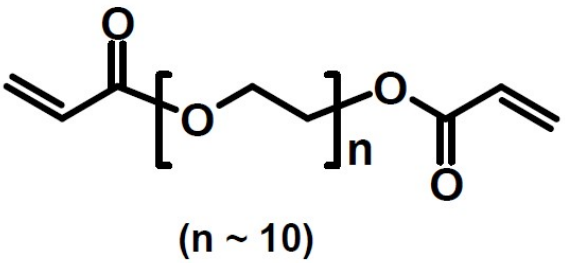


PETIA



(n ~ 10)

PEGDA

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