Supporting Information

PEG-based Cleavable Hydrogel Microparticles with controlled porosity for permiselective trafficking of biomolecular complexes in biosensing applications

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Table S1: Prepolymer solutions composition, in terms of PEGDA700 and DHEBA, and samples identification code.

NAME	PEGDA700 (w/v) %	DHEBA (w/v) %	R (mol PEG/mol Dheba)	X PEG	X DHEBA
15R40	15	0.1	42.9	0.98	0.02
15R4	15	1	4.29	0.81	0.19
10R40	10	0.07	40.8	0.98	0.02
10R4	10	0.7	4.08	0.81	0.19

Table S2: Flow rates and their ratio are imposed parameters; the capillary number Ca is calculated knowing the continuous phase properties and flow rate; mean droplet size and its standard deviation, frequency and spacing between two consequent droplets are obtained from the droplet generation videos analysis (Droplet Monitor software).

R	Q_d(µL/min)	Q_c(µL/min)	Size(µm)	S.Dev.(µm)	f (drops/s)	Spacing(µm)	Ca
10	0.25	2.5	75	2.4	19.9	110.2	3.03E-02
10	0.5	5	70.3	6.5	38.6	101.2	6.07E-02
20	0.1	2.0	73.2	1.17	9.7	157.8	2.43E-02

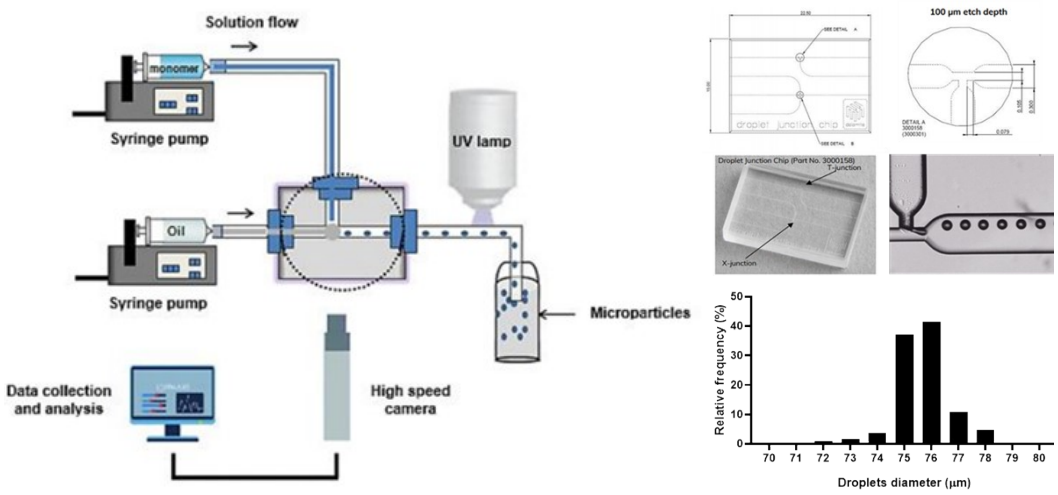

Figure S1: Left: Schematic illustration of the experimental microfluidic setup. Two syringe pumps push the solutions into the microfluidic channels, up to the T-junction where the droplet breakup occurs. Then the droplets are polymerized on flow in the outlet tube by means of an UV lamp and collected in a reservoir. A high-speed camera collects videos of the droplet formation and send the data to the software for the size and rate analysis; **Top Right:** Images and technical specification of the quartz hydrophobic droplet chip used for the W/O emulsion and an image of monodisperse droplets of 75 µm produced with the T-Junction chip; **Bottom right:** frequency distribution of droplets diameter evaluated from the video analysis of about 1000 droplets production (10R40).

Table S3: Microparticles' mean radius (µm) and standard deviation *pre*- and *post*- cleavage at 50 °C (overnight)

	Pre cleavage	Post cleavage
15R4	33.29 ± 1.04	36.78 ± 1.66
15R40	35.40 ± 1.34	39.65 ± 2.13
10R4	35.99 ± 1.51	41.51 ± 2.80
10R40	33.87 ± 1.19	38.66 ± 1.33

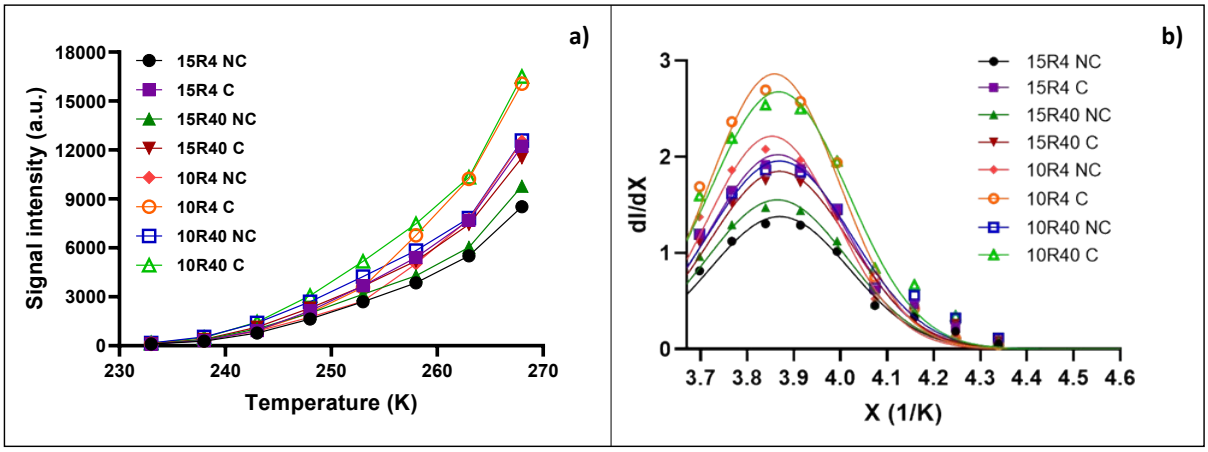

Figure S2: a) Variation of the NMR signal of water with the temperature for all the hydrogel compositions *pre*- and *post*-cleavage (IT curve); **b)** Derivative of the NMR signal with the inverse of temperature (K^{-1} = X, proportional to the pore radius) for all the hydrogel compositions.

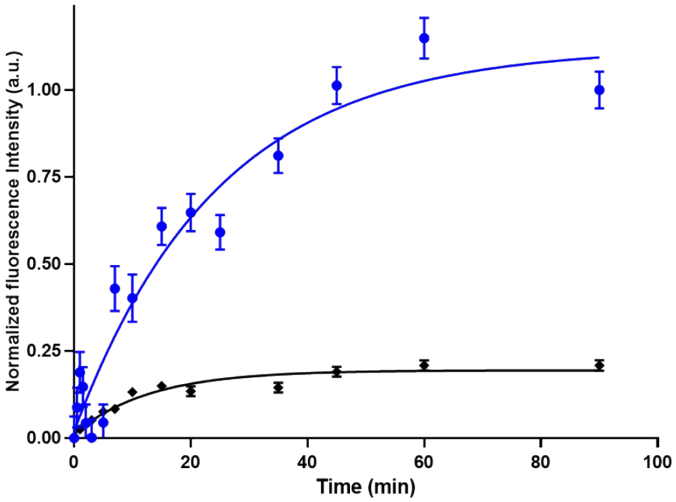

Figure S3: Diffusion kinetics of fluorescently labelled human IgG within 10R40 microparticles, before (black) and after the cleavage (blue).

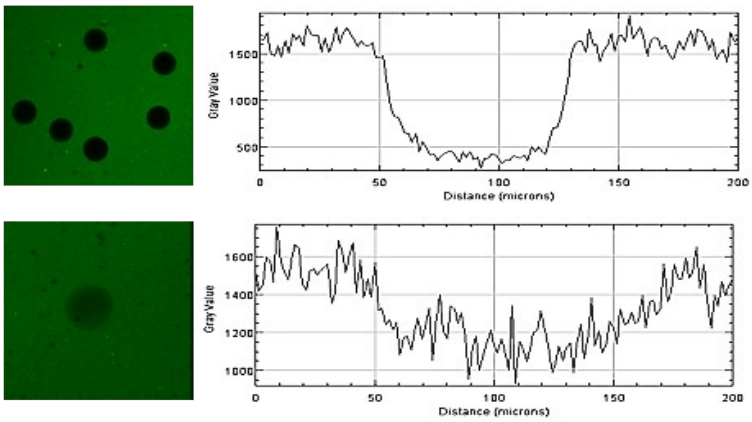

Figure S4: CLSM images and equilibrium fluorescence signal profile for the diffusion of a labelled IgG inside the 10R40 hydrogel microparticles, before (top) and after the cleavage (bottom);