Supporting Information

*i*3DP, a robust 3D printing approach enabling genetic post-printing surface modification

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Experimental:

Materials. 3D printer resin base was purchased from MiiCraft. All other chemicals and solvents were obtained from Sigma Aldrich and used as received except specially noted items. CuBr was purified by reflux in acetic acid. Initiator 2-(2-bromoisobutyryloxy) ethyl methacrylate (BrMA) and monomers, poly(ethylene glycol) methyl ether methacrylate (PEGMA, Average Mn 360) and 1H,1H,2H,2H-perfluorodecyl methacrylate (PFMA), were passed through an aluminum oxide column to remove inhibitors prior to use.

Preparation of initiator containing resin. To prepare the initiator containing resin, simply add BrMA into the resin base of MiiCraft 3D printer and mix well. After degasing for 30 min in dark, customized initiator containing resin was obtained. 5 wt% initiator containing resin were prepared and used for the following 3D printing.

Initiator integrated architectures created by 3D printing. MiiCraft 3D printer is built based on stereolithography, which creates 3D objects by photo-polymerizing the acrylate-based liquid resin in a layer-by-layer sequence. A solid 3D model is designed using CAD tool and digitally sliced into a series of 2D layers, which are then used to control the UV projection to solidify the liquid resin in a tank. Each time after one layer is solidified at the bottom of the tank, an elevator move downward to lifts it up and a new circle starts to solidify the next layer in the same way till the formation of the whole body of 3D object. For the 5 wt% initiator containing customized resin, the exposure time for each layer is 3.5 seconds, and the lift height is 50 μm. Actually, the parameters is the same to that for MiiCraft resin base, indicating the added initiators did not show any negative effect for the printing. Once finished, the printed architecture was ultrasonically rinsed by using ethanol to remove any physically absorbed resin and small molecular monomers, dried by nitrogen flow, and post cured by UV light for 15 min.

Surface-initiated atom transfer radical polymerization (SI-ATRP). For PEGMA, 4.4 g of PEGMA monomer and 10 mL of 1:4 (v:v) MeOH/H2O mixture were stirred in a flask under

nitrogen flow for 20 min; then 64 mg of 2,2-bipyridyl and 28 mg of CuBr were charged into a flask and purged with nitrogen flow again; 20 min later, *i*Lattices were added into the mixture. The polymerizations were then performed at room temperature under nitrogen protection for 2 h. For PFMA, 1.56 g of PFMA was added in 15 mL of DMF, and stirred under Argon flow for 20 min. Then, 78 mg of *N*,*N*,*N*′,*N*″,*N*‴-pentamethyldiethylenetriamine and 42 mg of CuBr were added to the solution. The mixture was then degassed under stirring and Argon flow for 20 min before syringing into Schlenk tube where *i*Lattices were already placed. 2 h of polymerization was conducted. After the polymerization, all the materials were rinsed with methanol and water under ultrasound, blew with nitrogen flow, and dried at 60 ^{o}C in vacuum overnight.

Characterization. Surface chemical composition information of 3D Lattices and iLattices was obtained by X-ray photoelectron spectroscopy (XPS). The measurement was carried out using a Kratos Axis Ultra spectrometer using a monochromatic Al Kα radiation source. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon. Using an Argon ion gun (Kratos Minibeam III) to etch the samples, the depth profile of *i*Lattice was measured. The Argon ion gun was operated at 4 kV and 15 mA emission current. The sputter area is 3 mm x 3 mm. The sputter rate is 1.3 nm per min for Al_2O_3, while the etching depth for polymer is estimated about 5 nm per min. The wettability was valued by directly dropping deionized water dyed by Rhodamine 6G onto the samples and recorded by Canon camera. The sessile water contact angles on flat surfaces were also measured by a Ramé-Hart Contact Angle Goniometer. The morphology of *i*Lattice and *i*Ball was investigated using a Hitachi S-4500 field emission scanning electro-microscope using a 5 kV accelerating voltage.

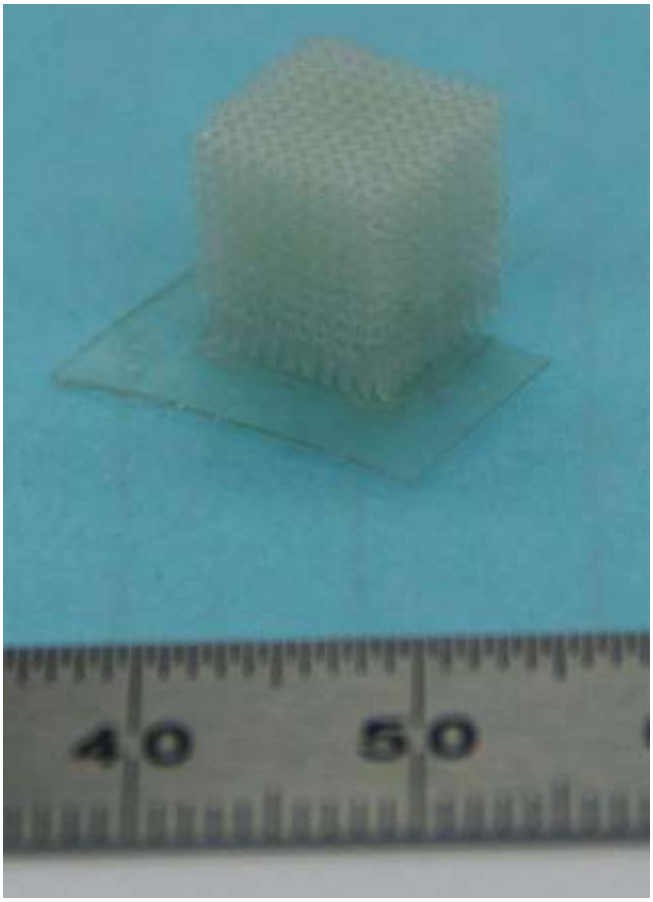

Fig. S1. Photograph of 3D printed *i*Lattice.

Table S1. Surface chemical composition of 3D printed Lattice and *i*Lattices

Samples	atom %[a]				
	C	O	P	Br	F
Lattice	75.3	21.2	3.5		
*i*Lattice	75.4	20.3	4.0	0.3	
poly(PFMA)-*i*Lattice	41.9 (42.4)[b]	5.0 (6.1)	0.0	0.1	53.0 (51.5)
poly(PEGMA)-*i*Lattice	70.6 (66.7)	29.1 (33.3)	0.2	0.2	

[a] The atom % was calculated by using XPS survey spectra. [b] The data shown in brackets are theoretical values.

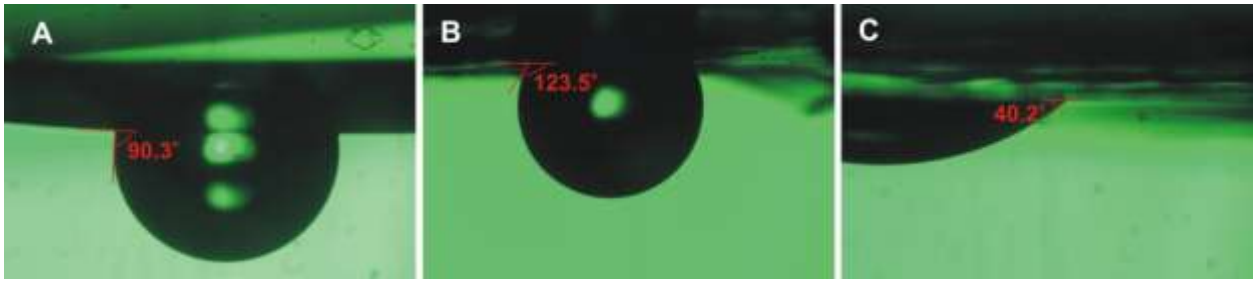

Fig. S2. Water contact angle of 3D printed flat film using 5 wt% BrMA customized resin before (A) and after poly(PFMA) (B) and poly(PEGMA) (C) grafting via SI-ATRP.

Movie S1 shows water droplets dropt on the poly(PEGMA) grafted *i*Lattice permeated into the network immediately.

Movie S2 shows water droplets dropt on the poly(PFMA) grafted *i*Lattice jumped away.

Movie S3 shows the sealed water inside the poly(PFMA)-*i*ball can be even freely rotated.