## **Microchamber Arrays Made of Biodegradable Polymers for Enzymatic Release of Small Hydrophilic Cargos**

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Figure S1. The Fraunhofer diffraction pattern imaging equipment. a) The specification of imaging equipment. The distance between the sample and the plain surface is 364 mm. The wavelength of laser light is 532 nm. A phone camera is fixed at the same position during all the imaging process. b) Images of acquiring diffraction patterns at darkened conditions.



S2. SEM 5(6)-carboxyfluorescein dye particles. a) Submicron size milled CF particles. b) Submicron size dye particles loaded into microwells of precoated PCL-PLA (1:2) patterned PDMS stamp. The diameter of each microwell is 10µm.



Figure S3. Calibration curve of 5(6)-carboxyfluorescein in PBS solutions. The fitting curve indicates the calibration curve is in an excellent linear line.



Figure S4. a,b) Schematic illustration of patterned silicon master (size: 1cm × 1cm) with micropillars (10 µm diameter, 4 µm height and a centre-to-centre distance of 30 µm) used in this work. c) SEM images of patterned silicon master. d) SEM images of patterned PDMS stamp made from the patterned silicon master.



Figure S5. Diffraction patterns of PCL microchamber arrays in different lipase concentration during degradation procedures.



Figure S6. SEM images of a layer of PCL film of different surface roughness on PDMS stamp after loading CF particle with dry powder loading method. a) PCL polymer layer formed with acetone as solvent. The CF particles are distributed both inside microwells and film surface which are unlikely to be swept away due to the rough surface. b) PCL polymer layer formed with chloroform as solvent. The CF particles only trapped inside microwells since the surface is smoother.



Figure S7. The wall thickness of microchambers and film thickness of microchamber array films of different polymers. a) FIB-SEM image of the wall thickness of PCL microchamber is about 2.3 μm. b) FIB-SEM image of the wall thickness of PCL-PLA (1:2) microchamber is about 1 μm. c) The thickness of the PCL microchamber array film is about 1.8 μm. d) The thickness of PCL-PLA (1:2) microchamber array film is about 1.6 μm.



Figure S8. Dye diffusion curve of PCL microchamber arrays encapsulated with 5(6)-carboxyfluorescein. Almost 75% of loaded dyes were leaked in the first 30 mins, indicating that PCL film could not prevent the leakage of small molecule dyes.



Figure S9. Encapsulation of 5(6)-CF in PCL-PLA (1:2) microchamber arrays. a,d) SEM images of precoated PDMS stamp before loading. b,e) SEM images of precoated PDMS stamp after loading 5(6)-CF dye particles. c,f) SEM images of PCL-PLA (1:2) microchamber arrays loaded with 5(6)-CF dye particles after sealing and printing.



Figure S10. PCL-PLA (1:2) microchamber arrays encapsulating 5,6-carboxyfluorescein inside microchambers. a-f) CLSM images of dye particles in microchamber arrays. g) 3D view of dye distribution. h) optical microscope image of PCL-PLA (1:2) microchamber arrays before dye loading. i) optical microscope image of PCL-PLA (1:2) microchamber arrays after dye loading.