Supporting Information

Optimization of 4D Polymer Printing Within a Massively Parallel Flow-Through Photochemical Microreactor

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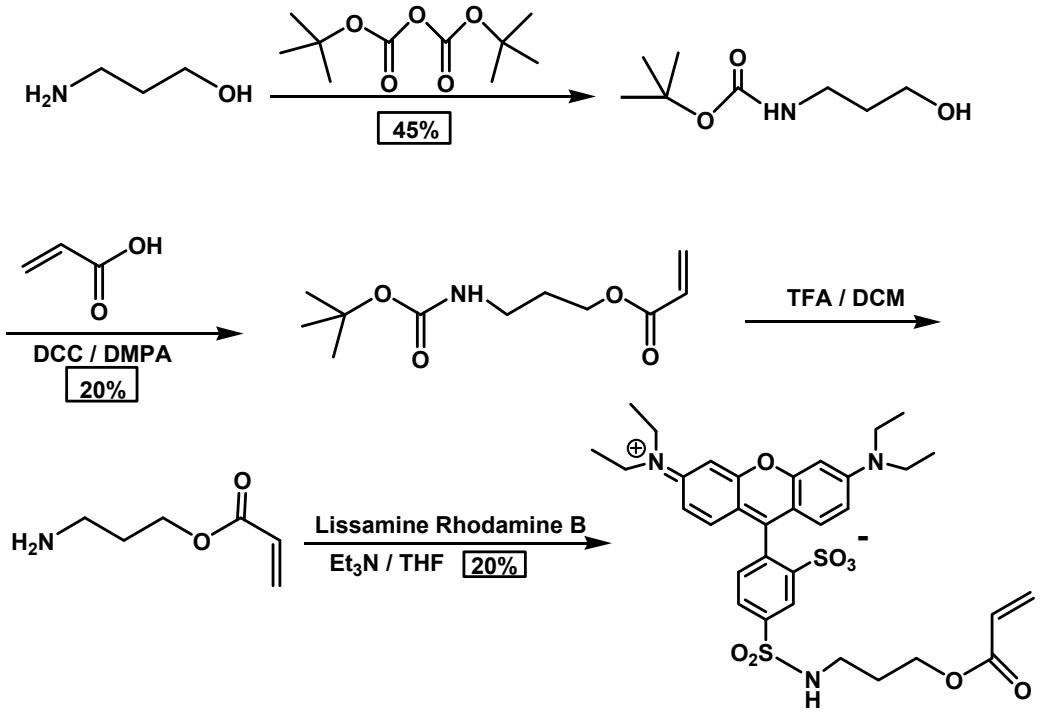
Table of Contents

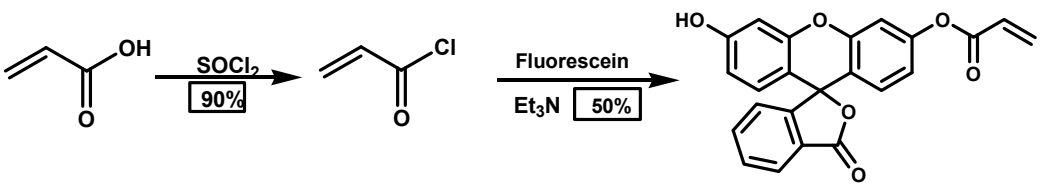
1. Organic synthesis and characterization

General methods. All solvents and reagents were purchased from Aldrich or VWR and solvents were dried prior to use following standard protocols. Thin layer chromatography was carried out using aluminum sheets pre-coated with silica gel 60 (EMD 40-60 μm, 230-240 mesh with 254 nm dye). All reactions were carried out under an inert N_2 atmosphere using standard Schlenk techniques or in a glove box unless otherwise noted. Compounds **1**,[1] **2**,[2] **3**,[3,4] were prepared according to previous published literature procedures. NMR spectra were obtained on a Bruker AVANCE 400 MHz spectrometer. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used as received. All chemical shifts are reported in ppm units with reference to the internal solvent peaks for ^{1}H and ^{13}C chemical shifts, and all spectral data were consistent with their reported literature values. High-resolution mass spectrometry analyses were carried out on an Agilent 6200 LC/MSD TOF system. Fluorescence emission spectra were obtained using a Shimadzu RF-5301/PC Spectro-fluoro-photometer. UV-Vis absorption spectra were obtained on Shimadzu α-1860A UV-Vis spectrometer.



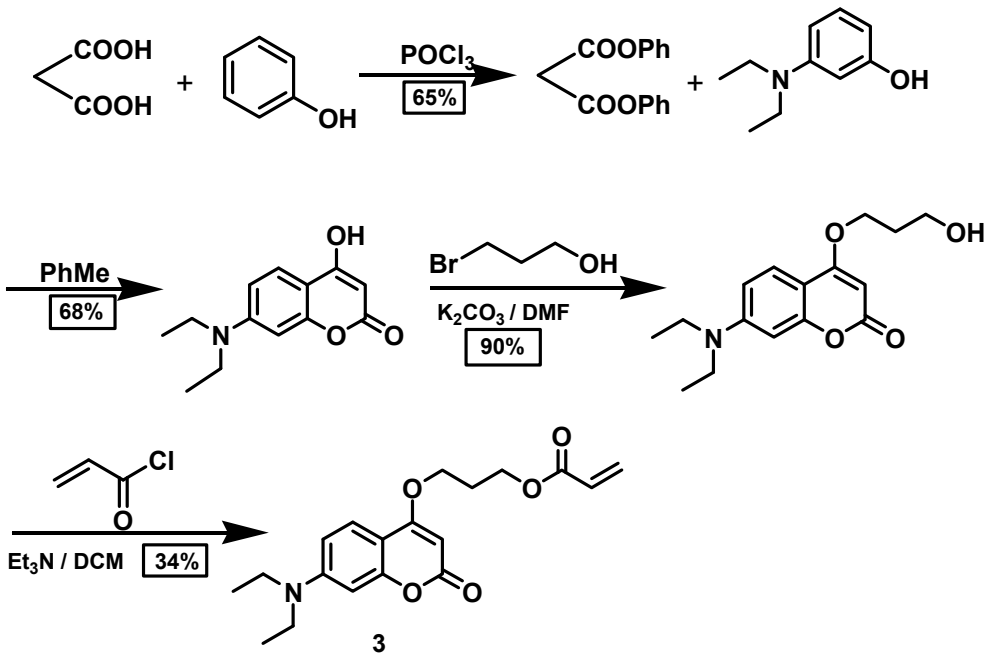
Scheme S1. Preparation of **1**.

1



2

Scheme S2. Preparation of **2**.



Scheme S3. Preparation of **3**.

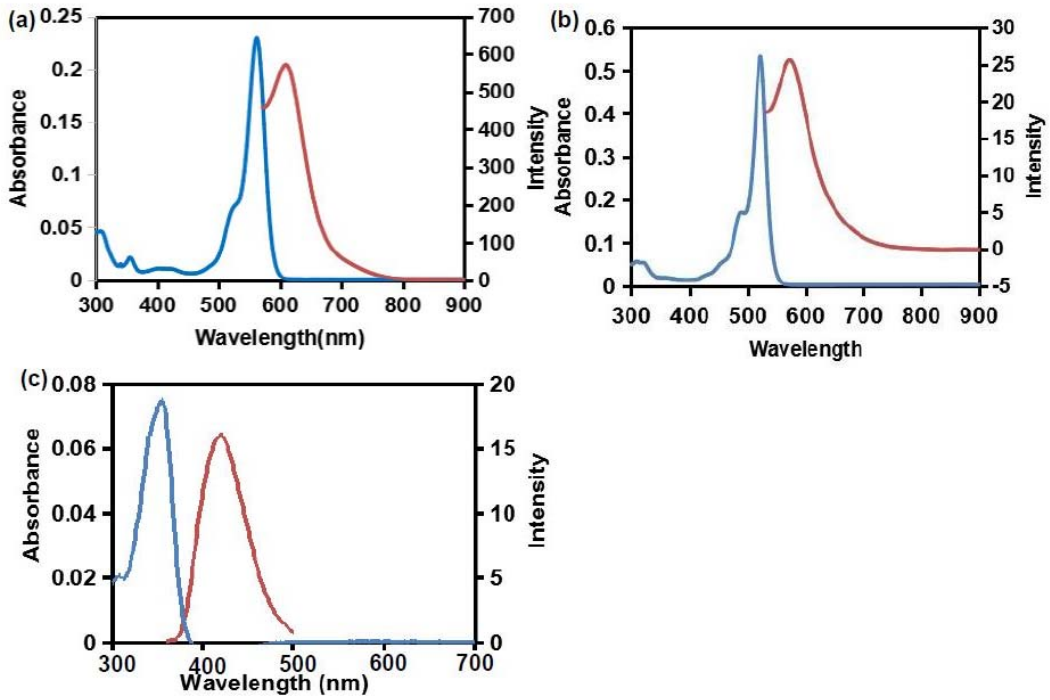
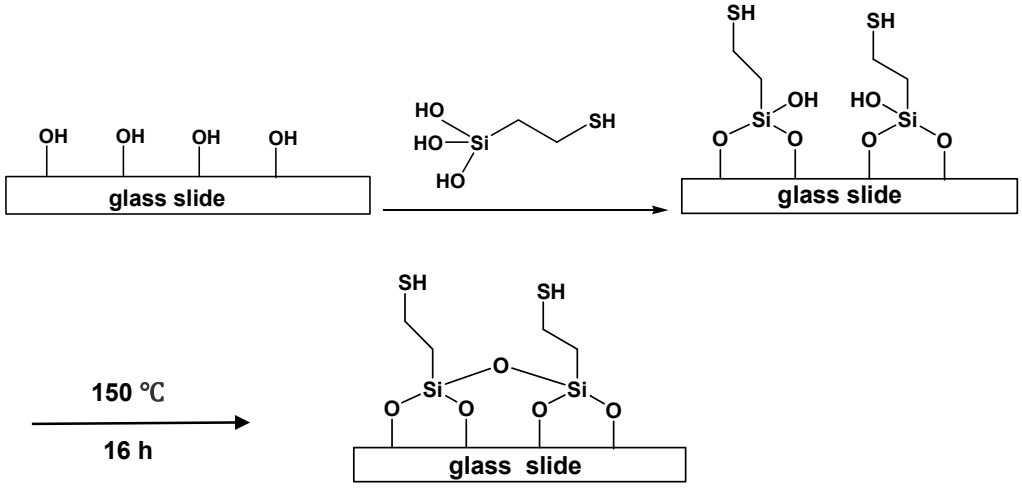


Figure S1. UV-Vis absorption (blue) and fluorescence emission (red) spectra of **1** (a), **2** (b), **3** (c).

2. Thiol-terminated glass slide preparation[5]

General methods. Microscope glass slides were purchased from VWR. All other chemicals and materials were purchased from Aldrich, VWR, or Gelest and used as received. Glass slides were cleaned by successively sonicating them (15 min) in 1 M HNO_3, H_2O, and EtOH solutions. After drying under a N_2 stream, the glass slides were incubated in a 20 ml vial containing 4.5 ml (3-Mercaptopropyl)trimethoxysilane (3-MPTS) in 120 ml toluene at 37 ^oC with mild agitation for 4 h. The glass slides were washed and rinsed with PhMe (2 ml), EtOH / PhMe (1:1) (2 ml), and EtOH (2 ml). Finally, the glass slides were cured in oven at 105 ^oC for 18 h and stored in MeOH at 4 ^oC until used.



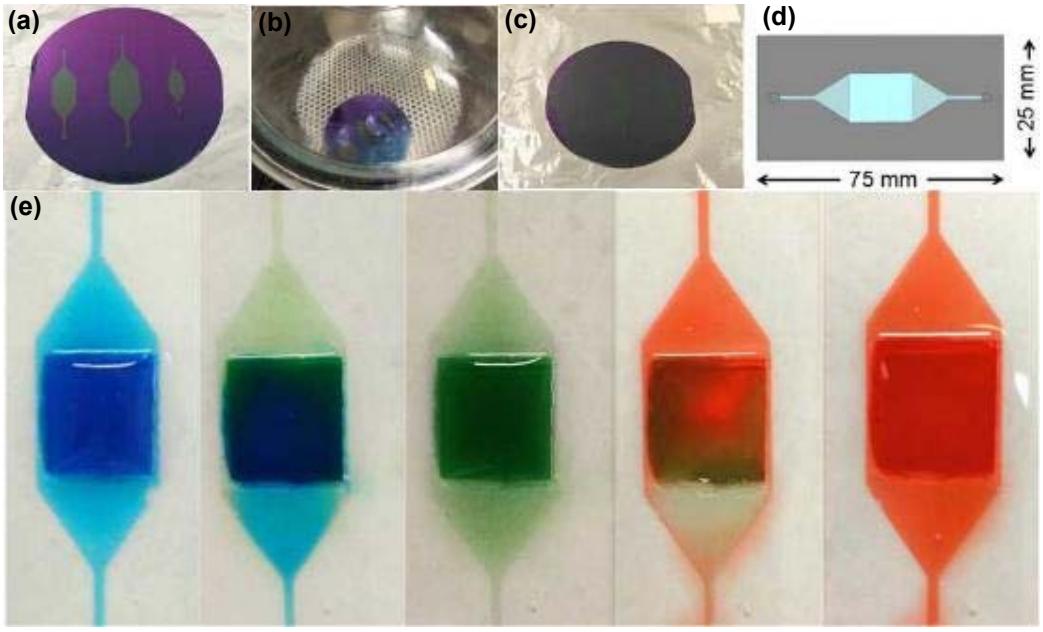
Scheme S4. Preparation of thiol-terminated glass slides.

3. Tip array preparation

General methods. PPL pen arrays with ~15000 pens and tip-to-tip spacing of 80 μm were prepared according to previously published literature reports.[6] To reduce adhesion of fluorescent inks to the elastomeric tips in the fluid cell, they were coated with a hydrophobic heptadecafluoro-1,1,2,2-tetra(hydrodecyl)trichlorosilane monolayer according to the procedure described below.

Heptadecafluoro-1,1,2,2-tetra(hydrodecyl)trichlorosilane coating on massively parallel pen arrays. Place the 1x 1 cm^2 tips array on a glass slide and expose to O_2 plasma (Harrick PDC-001) for 2 min at high power to grow a thin oxide layer. Add 50 μL heptadecafluoro-1,1,2,2-tetra(hydrodecyl)trichlorosilane to 2 mL PhMe in a glove box. Place the tip array and PhMe solution on opposite sides of a 12-inch diameter vacuum desiccator. Apply vacuum until the PhMe solution starts boiling. Leave the desiccator under static vacuum for 12 h. Add a new solution and repeat the coating procedure for another 12 h.

4. Fabrication of PDMS microfluidic cell



(f)

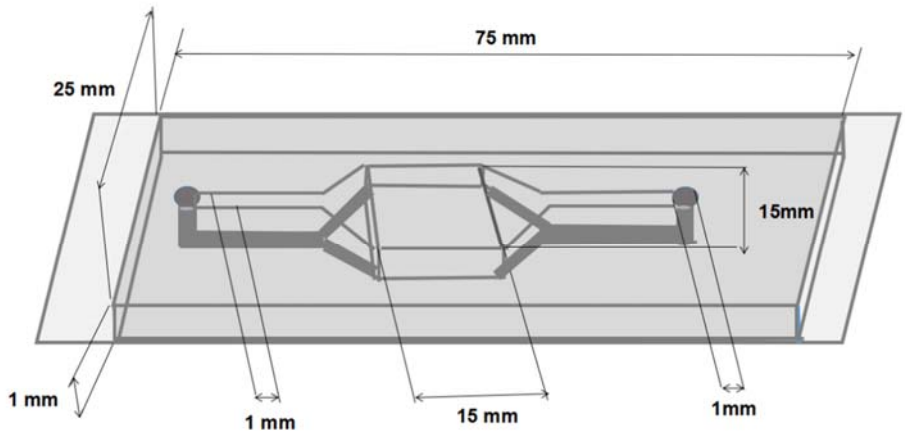


Figure S2. (a) Patterned Si(100) wafer mold for preparing three different sized PDMS microfluidic cells. (b) Coating the wafer with a heptadecafluoro-1,1,2,2-tetra(hydrodecyl)trichlorosilane in a vacuum dessicator. (c) Spin coat h-PDMS onto the wafer. (d) Dimensions of the PDMS microfluidic cell. (e) Display of the flow-through capabilities of the PDMS cell using blue, green, and orange dyes. (f) 3D mold design and construction of microfluidic cell. Microfluidic channel was a height of 500 μm and diameter 1 mm

General methods. All chemicals and materials were purchased from Aldrich, and were used as received. Specific reagents were prepared according to the previously published literature report.[6] The wafer mold for the fluid cells (Figure S2) was prepared by conventional Si-photolithography methods.[7] To create the fluid cell, place the patterned wafers in a glass petri dish and expose to O_2 plasma (Harrick PDC-001) for 2 min at high power to grow a thin oxide layer. Place the wafer on one side of a 12-inch diameter vacuum desiccator. Add 100 μL heptadecafluoro-1,1,2,2-tetra(hydrodecyl)trichlorosilane to 4 mL PhMe and place it on opposite sides of a 12-inch diameter vacuum desiccator. Apply vacuum until the PhMe solution starts boiling. Leave the desiccator under static vacuum for 24 h. Weight 17 g of h-PDMS precursor and 5.0 g of (25-35% (wt/wt) methylhydrosiloxane)-dimethylsiloxane copolymer in a

weighting boat and stir the mixture vigorously for 5 min using a plastic spatula. Put the weighing boat containing the prepolymer mixture into a desiccator and connect it to a vacuum line. Keep the desiccator under vacuum for 15 min to remove trapped air bubbles. Pour the copolymer on the prepared wafer, and ensure that the wafer was covered by the copolymer. Spin coat 5 g copolymer at 1000 rpm/s with a 300 rpm/s and check for the absence of bubbles. Place the master in a sealed container overnight at room temperature. After fully curing the copolymer, remove the PDMS film from the master. Place the fluid cell onto a clean microscope slide for storage.

5. Microfluidic Printer

General methods. Microfluidic components, including the microtubing, syringes, connectors, and bread boards, were purchased from LabSmith (USA). The components needed to build the flow through microfluidic device are listed in **Table S1**.

Table S1. Components required to construct the microfluidic cell.

#	Components
1	360 µm [0.014"] OD capillary tubing
2	Cape tite fittings kit
3	One piece fitting for 360 µm OD capillary tubing
4	One piece plug for 360 µm OD capillary tubing
5	Two piece fitting for 360 µm OD capillary tubing
6	Interconnect union for 360 µm OD capillary tubing
7	Interconnect cross for 360 µm OD capillary tubing
8	Union adapter for 360 µm OD capillary tubing
9	Needle connector for 360 µm OD capillary tubing
10	Standard breadboard 4’’× 6’’ platform for the fluid circuit
11	Lure lock disposable syringes

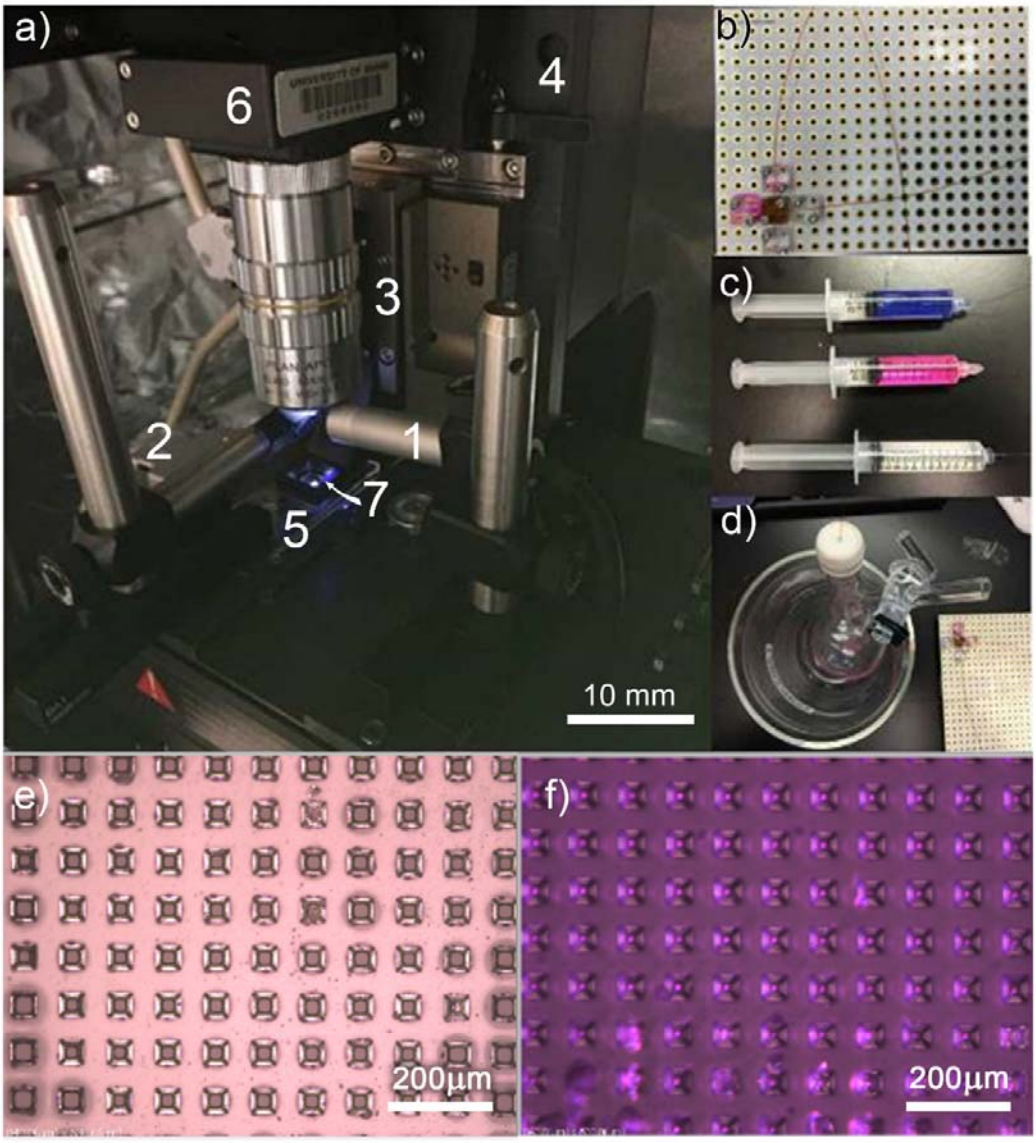

a)
6
4
3
2
1
7
5
10 mm
b)
c)
d)
e)
200µm
f)
200µm
g)
Relative Fluorescence (Counts)
210
180
150
120
90
60
30
0
100
200
300
400
500
Distance (µm)

Figure S3. (a) Microfluidic printer components ((1) UV light source. (2) Park System (3) z piezo actuator including z scanner, probe arm, probe head. (4) Lithography XE system. (5) PDMS cell placed on thiol-terminated surface. (6) Camera. (7) Pyramidal arrays attached to the tip carrier using regular glue and the tip carrier attached to the probe head. (b) Ink changing channel. (c) Ink reservoir connected to influx channel. (d) Outflux channel with a negative pressure device. (e) Pyramidal tips contact with ink film in chamber. (f) Light focus channel in contact with reactive surface in liquid phase. (g) Differences in light intensity across the pen array during illumination by 365 nm light (intensity : 42.74 mW/cm^2).

6. Printing of 1 on thiol-terminated glass surfaces by PPL

To confirm that the inks and glass surfaces could reproduce previous polymer patterning results, the printing procedure for creating patterns of grafted-from brush polymers of **1** on thiol-terminated glass slides was repeated following the previously reported protocol.[6] Briefly, PPL pen arrays with ~15000 pens and tip-to-tip spacing of 80 μm were exposed to O_2 plasma (Harrick PDC-001, 30 s, medium power, ~200 mTorr) to render their surfaces hydrophilic. 4 drops of the ink solution, comprised of **1** (1.2 mM, 0.8 mg), PEG (2,000 g/mol^{-1}, 5 mg/mL) and DMPA (0.30 mg, 1.17 mmol) were dissolved in 1 mL 80:20 THF : H_2O that was sonicated to ensure solution homogeneity. The ink mixture was spin coated (2,000 rpm, 2 min) onto the PPL pen array. A Park XE-150 scanning probe microscope (Park Systems Corp.) equipped with a PPL head, XEP custom lithography software, and an environmental chamber capable of controlling humidity were used for PPL patterning at a humidity of 78 % – 82 % at room temperature. The tip array was leveled by optical methods with respect to the substrate surface using an xy tilting stage. A dot array was printed by bringing the tip array into contact with the thiol- terminated glass surface, a 365 nm LED light with light intensity 42.74 mW/cm^{-2} was used in the patterning procedure with an exposure times 540 s. Light intensity was measured after reflection of the mirror with a intensity detector (General UV 513AB) and each measurement was record with same distance between the mirror and the detector. The surfaces were washed with EtOH (10 m) to remove excess ink, and patterns were imaged with fluorescence microscopy (Zeiss Axiovert-200, λ_{ex} = 562 nm, λ_{em} = 624 nm).

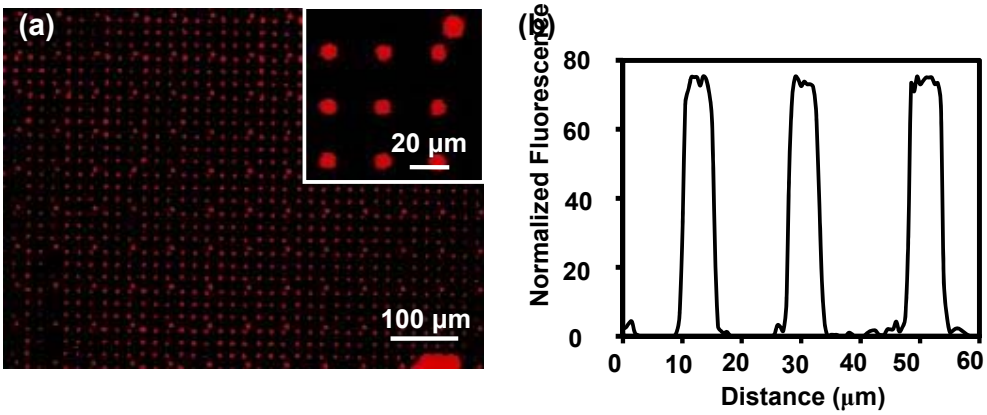


Figure S4. (a) Fluorescence microscopy image (Zeiss Axiovert-200, λ_{ex} = 562 nm, λ_{em} = 624 nm) with printing condition that DMPA/[**1**] = 1 in THF / H_2O (0.8: 0.2); light intensity 42.74 mW /cm^2 ; 365 nm UV light, exposure time 540 s; Z-extension －9 μm. (b) Intensity profile of the pattern is shown in the inset of (a).

7. Single spot single color printing within photochemical reactor

General methods. Massively parallel elastomeric tip arrays with ~15000 pens and tip-to-tip spacing of 80 μm were prepared following previously reported protocols.[6] A typical printing procedure is described, although in the systematic studies, solvents, concentrations of monomers, photoinitiator concentration, z-extension, reaction time, *t*, and light intensity were varied. Tips were covered with a single layer of heptadecafluoro-1,1,2,2-tetra(hydrodecyl)trichlorosilane to render the pen arrays hydrophobic following procedures identical to those described in section **S3**. Ink solutions containing DMPA (0.03 mg 0.117 mM) and **1** (0.8 mg 1.20 mM) were dissolved in 1 ml DMF. The fluid cell described in **Figure S4**. was placed onto a thiol-terminated glass surface. The surface was fixed onto the stage of a Park XE-150 scanning probe microscope (Park System Corp.) equipped with a PPL head and XEP custom lithography software. The elastomeric pen array was mounted onto the z- piezo of the AFM and localized on the top of microfluidic cell to seal the fluid cell. The tips array was leveled by optical methods with respect to the substrate surface using any *x*,*y* tilting stage. A dot array was printed by bringing the tip array into contact with the thiol-terminated glass surface, introducing the ink solution into the solution cell, and varying

the light intensity, exposure time, [DMPA]/[**1**] ratio and Z-piezo extension, with the point at which the tips first contact the surface considered z=0. Light intensity was measured after reflection off of the mirror with a light intensity detector (General UV 513AB), and each measurement was recorded with same distance between the mirror and the detector. All fluorescence images were observed under a fluorescence microscopy Zeiss Axiovert-200 and processed with Axioversion Rel. 4.8. Light sources was provided by with Rhodamine channel (λ_{ex} = 562 nm, λ_{em} = 624 nm). Feature size was determined as the average of 20 s spots and error is defined as the standard deviation from the average. The edge of feature was used *image-J* signal- to – background plot and the feature edge is defined as the points at which fluorescence decrease 90% from the maximum.

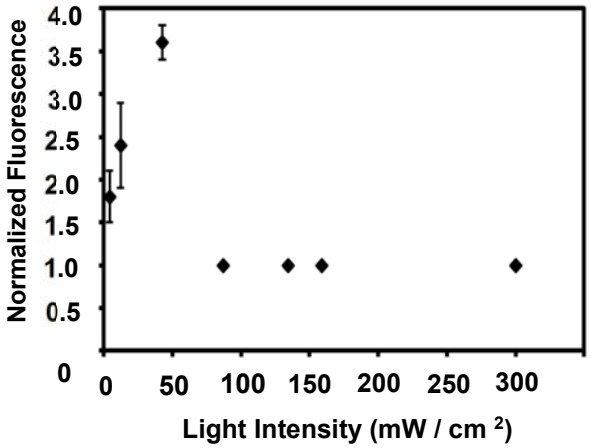
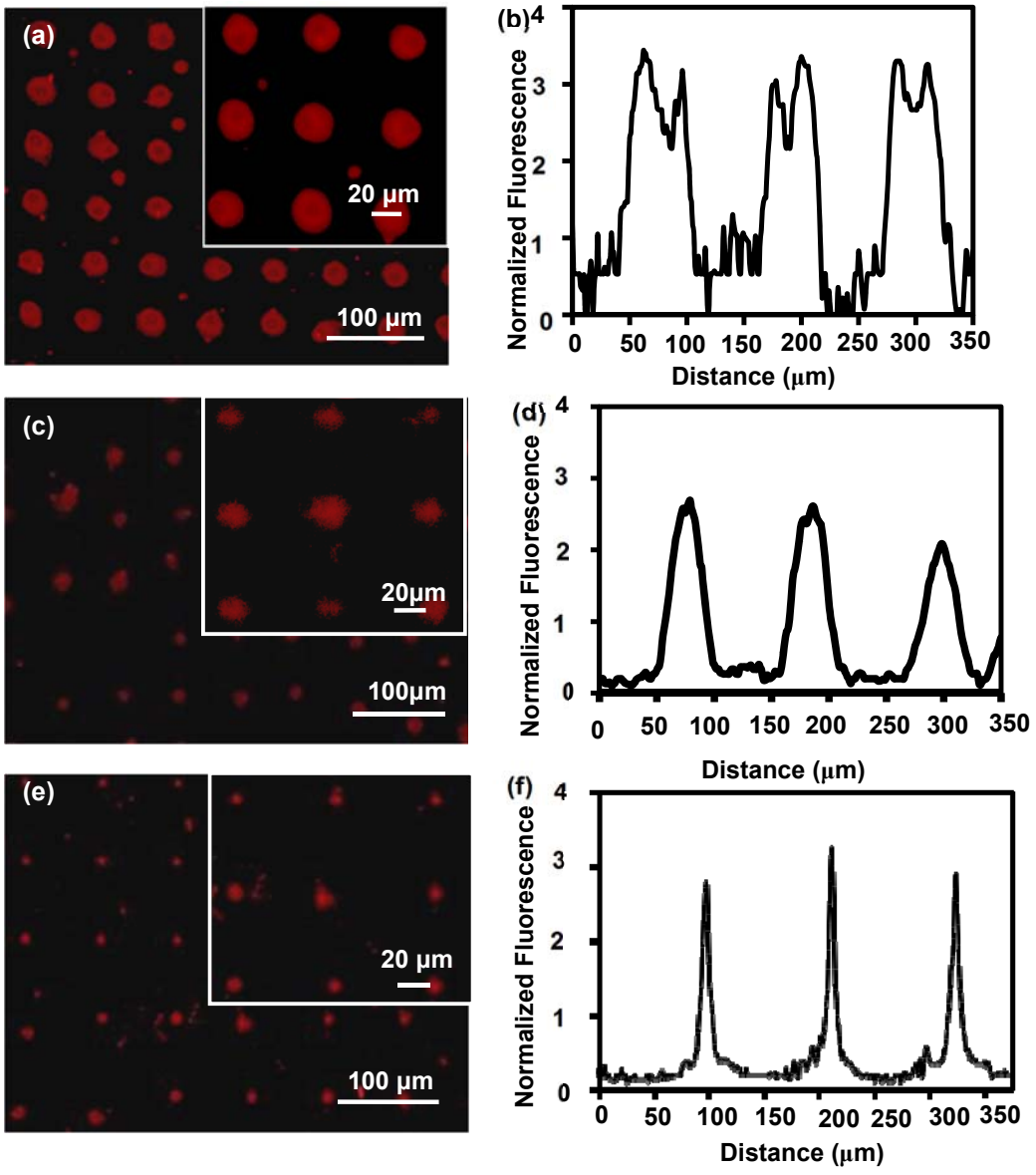


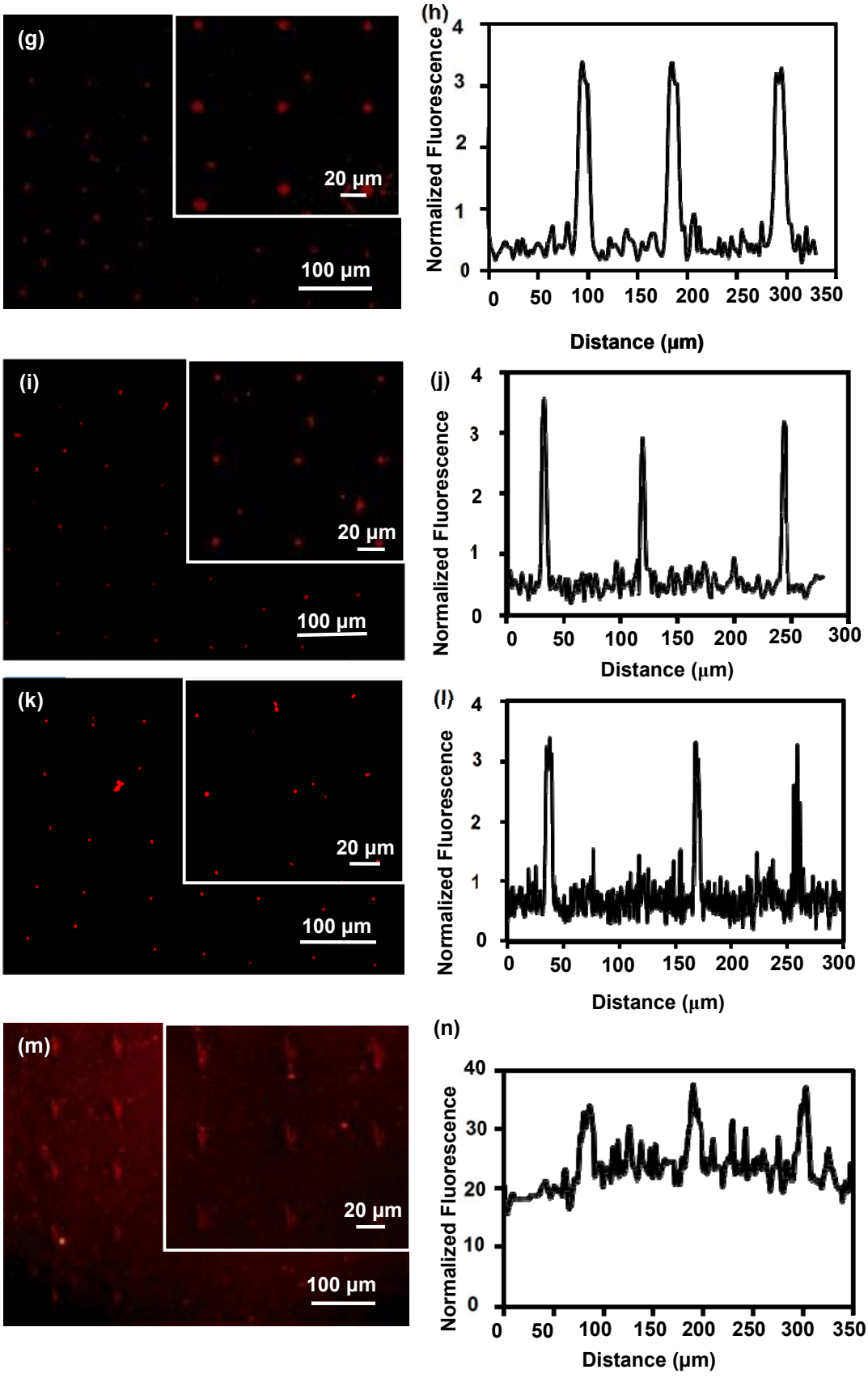
Figure S5. Effect of light intensity on normalized fluorescence of single spot printing **1** within massively paralleled nanoreactor with printing conditions: *t* 360s; [DMPA] /[**1**] = 0.1 and varying light intensity from 4.3 mW/cm^2 to 300 mW/cm^2.

Table S2. Optimization of single spot printing of poly(**1**) within the massively parallel microfluidic photochemical nanoreactor. The reaction parameters that were systematically varied were photoinitiator concentration, [DMPA], the monomer concentration [**1**], the reaction time, *t*, the light intensity, the z-piezo extension, Z-extend, and the normalized fluorescence, S/B.

#	Solvent	[DMPA] (mM)	[1] (mM)	*t* (s)	Light Intensity (mW/cm^2)	Z-Extend (μm)	S/B
1	DMF	2.34	2.98	30	42.74	−9	1
2	DMF	2.34	2.98	60	42.74	−9	1.1±0.14
3	DMF	2.34	2.98	120	42.74	−9	1.3±0.06
4	DMF	2.34	2.98	180	42.74	−9	1.41±0.1
5	DMF	2.34	2.98	300	42.74	−9	1
6	DMF	2.34	2.98	30	86.93	−9	1
7	DMF	2.34	2.98	60	86.93	−9	1.28
8	DMF	2.34	2.98	90	86.93	−9	1.37
9	DMF	2.34	2.98	180	86.93	−9	1.31
10	DMF	2.34	2.98	300	86.93	−9	1.38
11	DMF	1.17	1.2	360	42.74	−9	1.5±0.1
12	DMF	1.17	1.2	360	42.74	−9	1.5±0.1
13	DMF	1.17	1.2	360	42.74	−9	1.5±0.05
14	DMF	0.117	1.2	360	86.93	−9	1
15	DMF	0.117	1.2	360	134.7	−9	1
16	DMF	0.117	1.2	360	158.9	−9	1
17	DMF	0.117	1.2	360	300	−9	1
18	DMF	0.117	1.2	360	42.74	−9	3.6±0.2
19	DMF	0.117	1.2	360	4.3	−9	1.8±0.3
20	DMF	0.117	1.2	360	12.34	−9	2.4±0.5
21	DMF	0.117	1.2	0	42.74	−9	1
22	DMF	0.117	1.2	60	42.74	−9	1
23	DMF	0.117	1.2	180	42.74	−9	1
24	DMF	0.117	1.2	300	42.74	−9	1.7±0.8
25	DMF	0.117	1.2	420	42.74	−9	4.5±0.4
26	DMF	0.117	1.2	540	42.74	−9	8.75±0.5
27	DMF	0.117	1.2	660	42.74	−9	2.5±0.8
28	DMF	0.117	1.2	780	42.74	−9	1.3±0.16
29	DMF	0.117	1.2	900	42.74	−9	1
30	DMF	0.117	1.2	540	42.74	−16	7.2±0.64
31	DMF	0.117	1.2	540	42.74	−12	10.4±4.5
32	DMF	0.117	1.2	540	42.74	−9	8.3±0.74
33	DMF	0.117	1.2	540	42.74	−6	5.9±0.53
34	DMF	0.117	1.2	540	42.74	−3	4.5±0.56
35	DMF	0.117	1.2	540	42.74	−2	4.5±0.4
36	DMF	0.117	1.2	540	42.74	0	1.6±0.14
37	DMF	0.117	1.2	540	42.74	2	2.2±0.32

38	DMF	0.00117	1.2	540	42.74	−9	1
39	DMF	0.0059	1.2	540	42.74	−9	1
40	DMF	0.0117	1.2	540	42.74	−9	5±0.54
41	DMF	0.059	1.2	540	42.74	−9	5.9±0.32
42	DMF	0.117	1.2	540	42.74	−9	8.3±0.74
43	DMF	0.23	1.2	540	42.74	−9	2.1±0.16
44	DMF	0.59	1.2	540	42.74	−9	1.2±0.15
45	DMF	1.17	1.2	540	42.74	−9	1
46	DMF	5.9	1.2	540	42.74	−9	1
47	DMF	11.7	1.2	540	42.74	−9	1




(g)
20 μm
100 μm
(h)
Normalized Fluorescence
Distance (μm)
(i)
20 μm
100 μm
(j)
Normalized Fluorescence
Distance (μm)
(k)
20 μm
100 μm
(l)
Normalized Fluorescence
Distance (μm)
(m)
20 μm
100 μm
(n)
Normalized Fluorescence
Distance (μm)

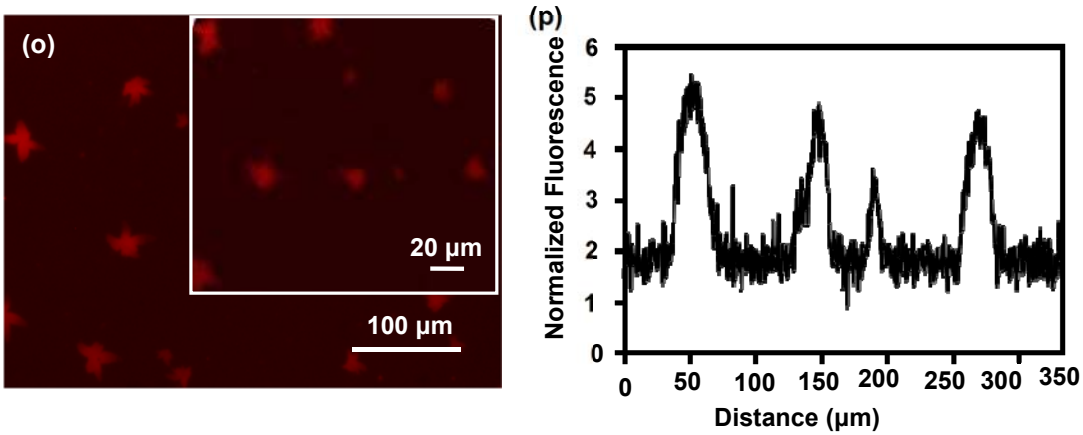
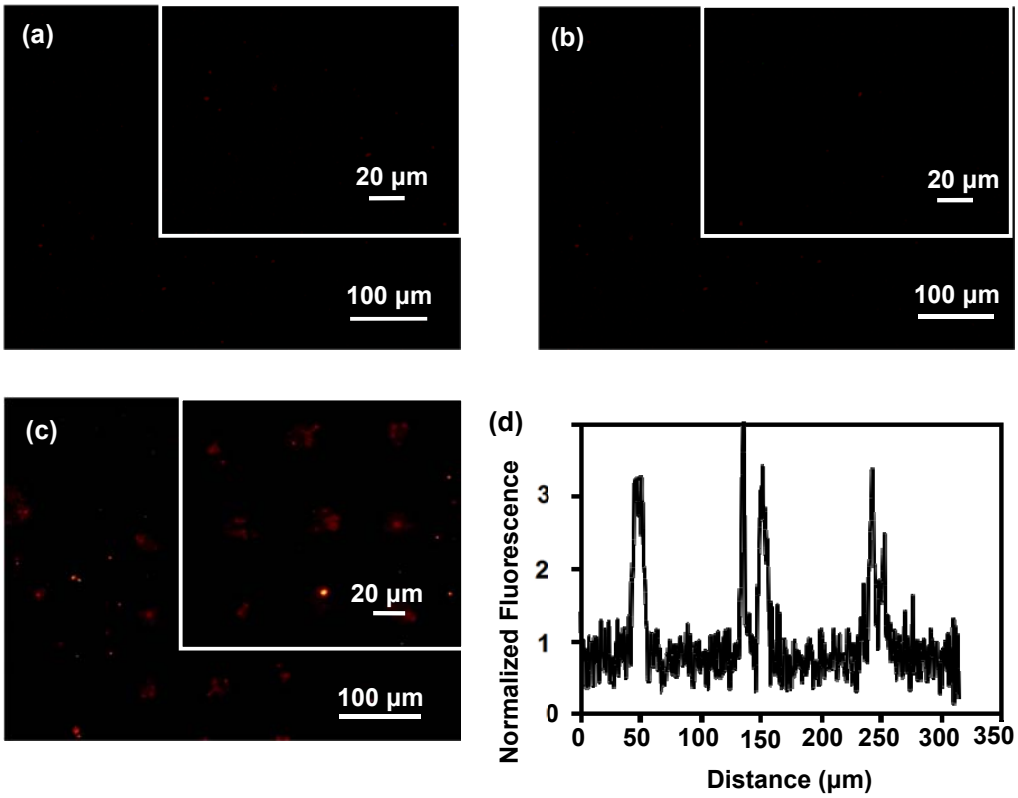


Figure S6. (a,c,e,g,i,k,m,o) Fluorescence microscopy image (Zeiss Axiovert-200, λ_{ex} = 562 nm, λ_{em} = 624 nm) with printing condition of [DMPA]/[**1**] = 0.1 in DMF; light intensity 42.74 mW /cm^2 ; 365 nm UV light; exposure time 540 s; varying Z extension from – 16, -12, -9, -6, -3 , -2, 0, +2 . (b,d,f,h,j,l,n,p) Intensity profiles of normalized fluorescence across arrays of poly(**1**).



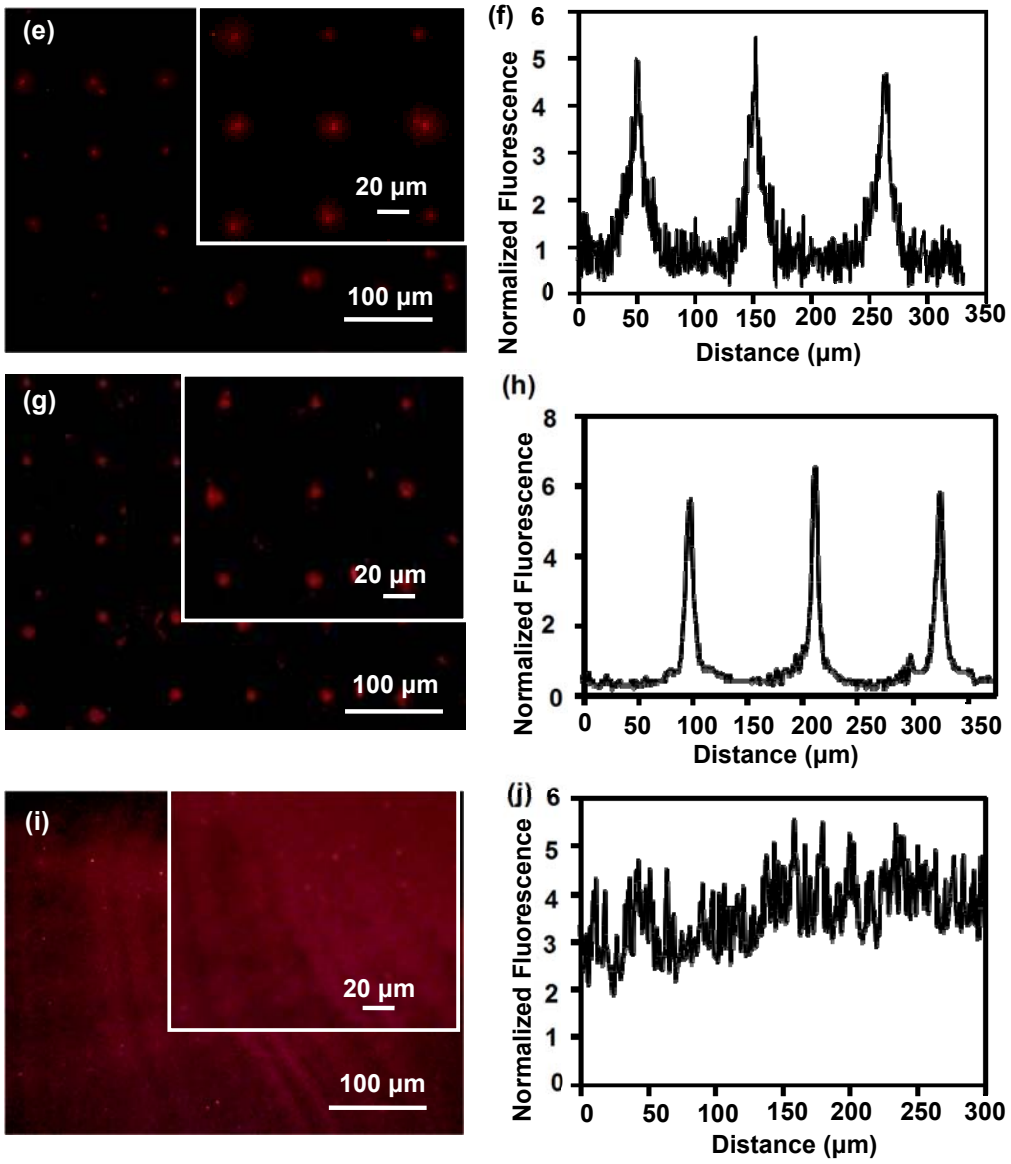
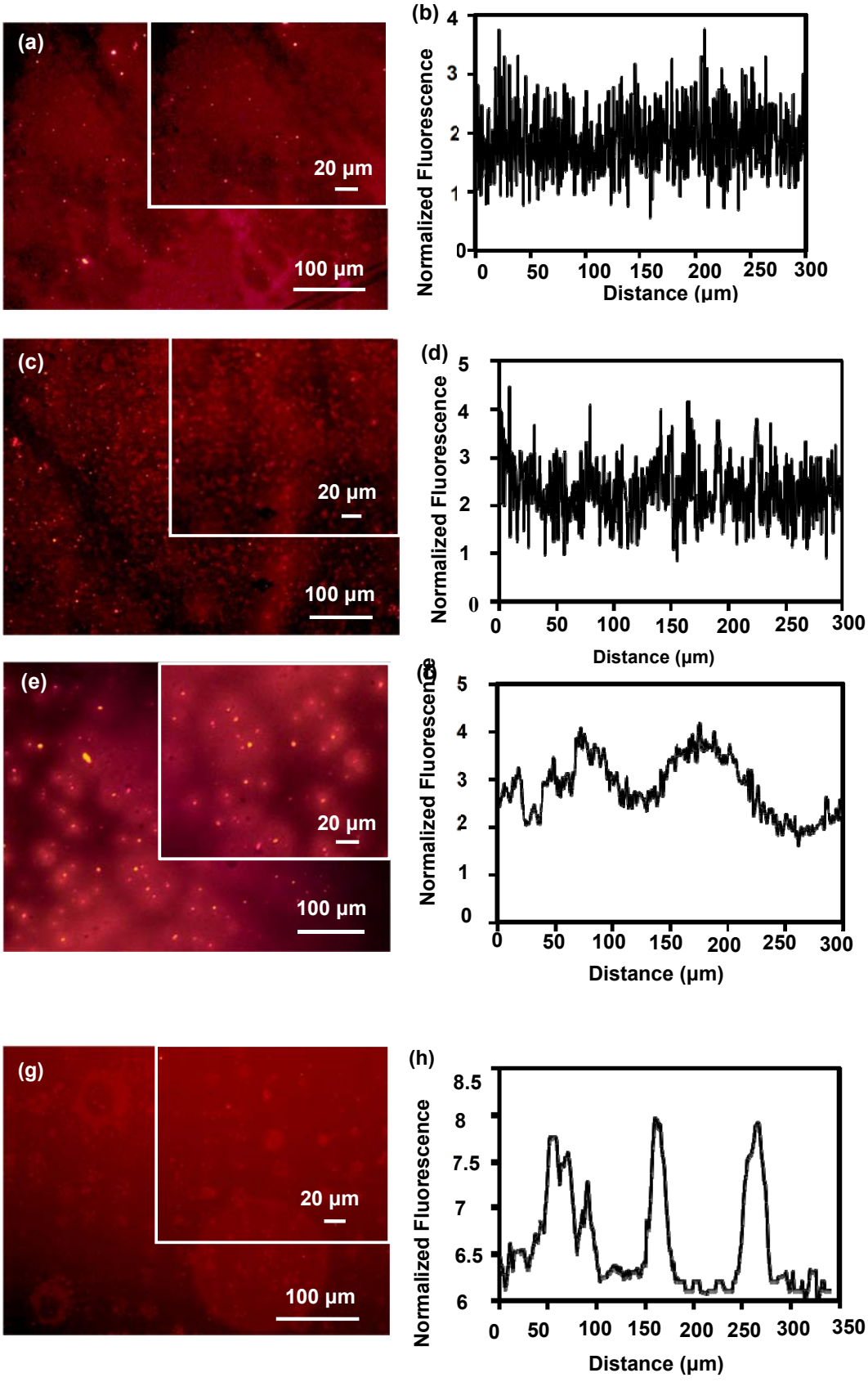


Figure S7. (a,c,e,g,l) Fluorescence microscopy image (Zeiss Axiovert-200, λ_{ex} = 562 nm, λ_{em} = 624 nm) with printing condition of [DMPA]/[**1**] = 0.1 in DMF; light intensity 42.74 mW /cm^2 ; 365 nm UV light, exposure time 0, 180, 300, 420, 480, 540, 660, 900 s, Z extend height ─ 9 μm. (d,f,h,j) Intensity profile of the inset of normalized fluorescence across arrays of poly (1).


(a)
20 μm
100 μm
(b)
Normalized Fluorescence
Distance (μm)
(c)
20 μm
100 μm
(d)
Normalized Fluorescence
Distance (μm)
(e)
20 μm
100 μm
(f)
Normalized Fluorescence
Distance (μm)
(g)
20 μm
100 μm
(h)
Normalized Fluorescence
Distance (μm)

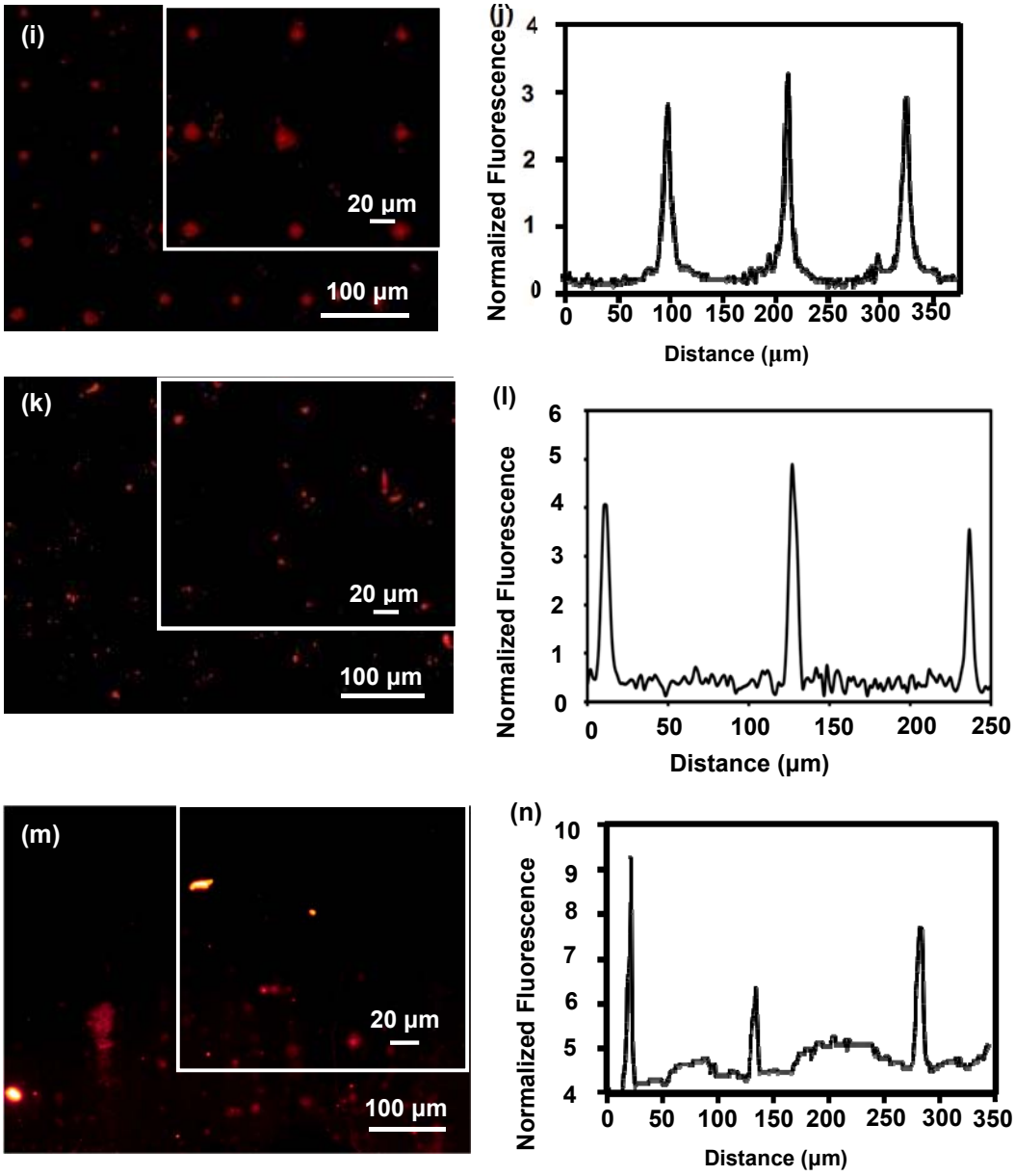


Figure S8. (a,c,e,g,l,k,m) Fluorescence microscopy image (Zeiss Axiovert-200, λ_{ex} = 562 nm, λ_{em} = 624 nm) with printing condition that [DMPA]/[**1**] =10, 1, 0.5, 0.2, 0.1, 0.01, 0.005 in DMF; light intensity 42.74 mW / cm^2 ; 365 nm UV light; exposure time 540 s; Z extend height with -9 μm. (b,d,f,h,j,l,n) Intensity profile of the inset of normalized fluorescence across arrays of poly(**1**).

8. Multi-spot single color printing within photochemical reactor

General methods. Massively parallel elastomeric tip arrays with ~15000 pens and tip-to-tip spacing of 80 μm were prepared following previously reported protocols.[6] A typical printing procedure is described, although in the systematic studies, solvents, concentrations of monomers, photoinitiator concentration, z-extension, reaction time, *t*, and light intensity were varied. Tips were covered with a single layer of heptadecafluoro-1,1,2,2-tetra(hydrodecyl)trichlorosilane to render the pen arrays hydrophobic following procedures identical to those described in section **S3**. Ink solutions containing DMPA (0.03 mg 0.117 mM) and **1** (0.8 mg 1.20 mM) were dissolved in 1 ml DMF. The fluid cell described in **Figure S2**. was placed onto a thiol-terminated glass surface. The surface was fixed onto the stage of a Park XE-150 scanning probe microscope (Park System Corp.) equipped with a PPL head and XEP custom lithography software. The elastomeric pen array was mounted onto the z- piezo of the AFM and localized on the top of microfluidic cell to seal the fluid cell. The tips array was leveled by optical methods with respect to the substrate surface using any x,y tilting stage. A multi-spots arrays were printed by bringing the tip array into contact with the thiol-terminated glass surface, introducing new ink solution into the solution cell after each spot printed on the glass surface, and varying the massively tips array x, y moving speed, exposure time, and Z-piezo lift height, with the optimum Z-piezo extension, [DMPA]/[1] ratio, light inte Light intensity was measured after reflection off of the mirror with a light intensity detector (General UV 513AB), and each measurement was recorded with same distance between the mirror and the detector. Multi-spots array in **Table S4.** defined that the coordination of each spot to be (-35, 35), spot 2 (0, 35), spot 3 (-35, 0), spot 4 (0,0). All fluorescence images were observed under a fluorescence microscopy Zeiss Axiovert-200 and processed with Axioversion Rel. 4.8. Light sources was provided by with Radanmine channel (λ_{ex} = 562 nm, λ_{em} = 624 nm).

Table S3. Optimization of multispot printing of poly(**1**) within the massively parallel microfluidic photochemical nanoreactor. The reaction parameters that were systematically varied were photoinitiator concentration, [DMPA], the monomer concentration, [**1**], the reaction time, *t*, the light intensity, the z-piezo extension, z-Extend, height of z-piezo lift between spots, and massively tip arrays moving speed in the XY direction between spots. Is a complete pattern obtained, Complete, the normalized fluorescence, S/B.

#	Solvent	[DMPA] (mM)	[1] (mM)	*t* (s)	Intensity (mW/cm^2)	Extend (μm)	Z Left (um)	XY Speed (μm/s)	Contr olled	Array	Comp lete	S/B
48	DMF	0.117	1.2	60	42.74	−9	10	0.5	No	3X3	No	1
49	DMF	0.117	1.2	60	42.74	−9	10	2	No	3X3	No	1
50	DMF	0.117	1.2	60	42.74	−9	10	5	No	3X3	No	1
51	DMF	0.117	1.2	60	42.74	−9	10	10	No	3X3	No	1
52	DMF	0.117	1.2	60	42.74	−9	10	15	No	3X3	No	1
53	DMF	0.117	1.2	60	42.74	−9	10	10	No	3X2	No	1
54	DMF	0.117	1.2	70	42.74	−9	10	10	No	3X2	No	1
55	DMF	0.117	1.2	80	42.74	−9	10	10	No	3X2	No	1
56	DMF	0.117	1.2	90	42.74	−9	10	10	No	3X2	No	1
57	DMF	0.117	1.2	60	42.74	−9	10	10	No	2X2	No	1
58	DMF	0.117	1.2	70	42.74	−9	10	10	No	2X2	No	1
59	DMF	0.117	1.2	80	42.74	−9	10	10	No	2X2	No	1
60	DMF	0.117	1.2	90	42.74	−9	10	10	No	2X2	No	1
61	DMF	0.117	1.2	120	42.74	−9	10	10	No	2X2	No	1
62	DMF	0.117	1.2	140	42.74	−9	10	10	No	2X2	No	1
63	DMF	0.117	1.2	45x2	42.74	−9	1000	10	yes	2X2	No	1
64	DMF	0.117	1.2	60x2	42.74	−9	1000	10	yes	2X2	No	1
65	DMF	0.117	1.2	70x2	42.74	−9	1000	10	yes	2X2	No	1
66	DMF	0.117	1.2	90x2	42.74	−9	1000	10	yes	2X2	Yes	2.3± 0.2
67	DMF	0.117	1.2	100,90,80	42.74	−9	1000	10	yes	3X2	No	1
68	DMF	0.117	1.2	45x2	42.74	−9	1000	10	yes	3x2	No	1
69	DMF	0.117	1.2	70x2	42.74	−9	1000	10	yes	3x2	Yes	4.5
70	DMF	0.117	1.2	90x2	42.74	−9	1000	10	yes	3X2	Yes	3.8
71	DMF	0.117	1.2	140x2	42.74	−9	1000	10	yes	3x2	Yes	4
72	DMF	0.117	1.2	140	42.74	−9	1000	10	yes	2x2	Yes	2.0±0.4
73	DMF	0.117	1.2	360	42.74	−9	1000	10	yes	2x2	Yes	2.8±0.3
74	DMF	0.117	1.2	420	42.74	−9	1000	10	yes	2x2	Yes	4.0±0.1
75	DMF	0.117	1.2	480	42.74	−9	1000	10	yes	2x2	Yes	5.8±0.2
76	DMF	0.117	1.2	600	42.74	−9	1000	10	yes	2x2	Yes	1.6±0.12

Table S4. Multispot printing of poly(**1**) within the massively parallel microfluidic photochemical nanoreactor. Parameter settings for data in **Figure 3**.

#	Solvent	[DMPA] (mM)	[1] (mM)	t (s)	Intensity (mW/cm^2)	Extend (μm)	Z Left (μm)	Static Ink	Controlled	Array	Complete	S/B
77	DMF	0.117	1.2	660	42.74	−9	100	No	yes	2x2	Yes	1.1±0.06
78	DMF	0.117	1.2	540	42.74	−9	100	No	yes	2x2	Yes	1.9±0.2
79	DMF	0.117	1.2	480	42.74	−9	100	No	yes	2x2	Yes	7.3±0.2
80	DMF	0.117	1.2	420	42.74	−9	100	No	yes	2x2	Yes	4.7±0.2
81	DMF	0.117	1.2	360	42.74	−9	100	No	yes	2x2	Yes	2.9±0.5
82	DMF	0.117	1.2	140	42.74	−9	100	No	yes	2x2	Yes	2.0±0.03
83	DMF	0.117	1.2	660	42.74	−9	100	yes	yes	2x2	Yes	1.4±0.7
84	DMF	0.117	1.2	540	42.74	−9	100	yes	yes	2x2	Yes	2.4±2.0
85	DMF	0.117	1.2	480	42.74	−9	100	yes	yes	2x2	Yes	4.8±1.6
86	DMF	0.117	1.2	420	42.74	−9	100	yes	yes	2x2	Yes	4.2±1.7
87	DMF	0.117	1.2	360	42.74	−9	100	yes	yes	2x2	Yes	2.7±0.6
88	DMF	0.117	1.2	140	42.74	−9	100	yes	yes	2x2	Yes	2.1±0.8

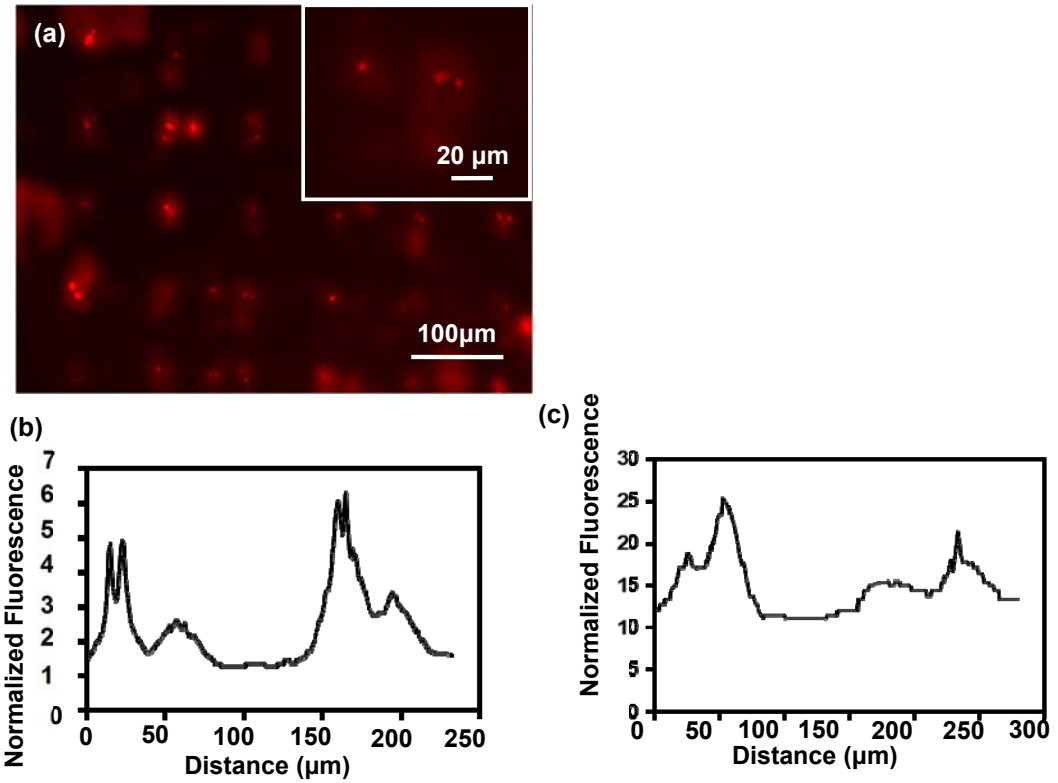


Figure S9. (a) Fluorescence microscopy image (Zeiss Axiovert-200, λ_{ex} = 562 nm, λ_{em} = 624 nm) with printing condition that [DMPA]/[**1**] = 0.1 in DMF; light intensity 42.74 mW / cm^2 ; 365 nm UV light; exposure time 140 s; Z extend height with -9 μm. (b) Intensity profile of spot (1,1) and (0,1) in the inset. (c) Intensity profile of spot (-1,0) and (0,0) in the inset.

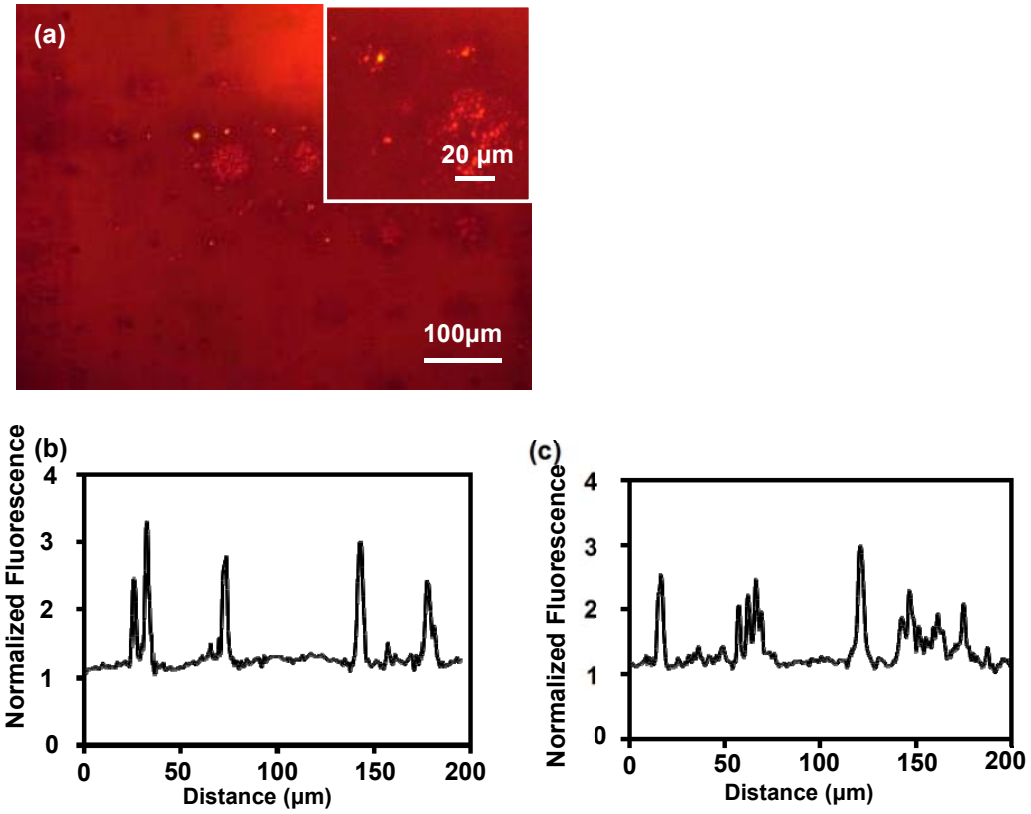
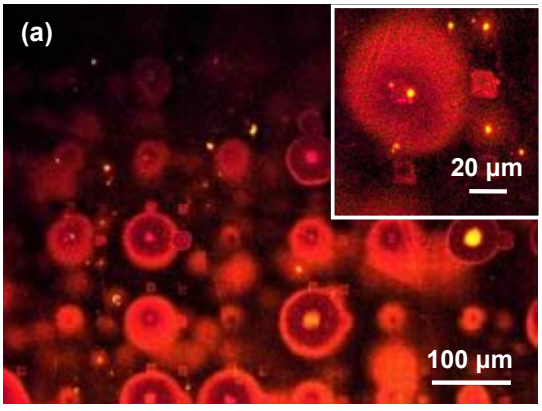


Figure S10. (a) Fluorescence microscopy image (Zeiss Axiovert-200, λ_{ex} = 562 nm, λ_{em} = 624 nm) with printing condition that [DMPA]/[**1**] = 0.1 in DMF; light intensity 42.74 mW/cm^{-2}; 365 nm UV light with exposure time 360 s; Z extend height with -9 μm. (b) Intensity profile of spot (1,1) and (0,1) in the inset. (c) Intensity profile of spot (-1,0) and (0,0) in the inset.



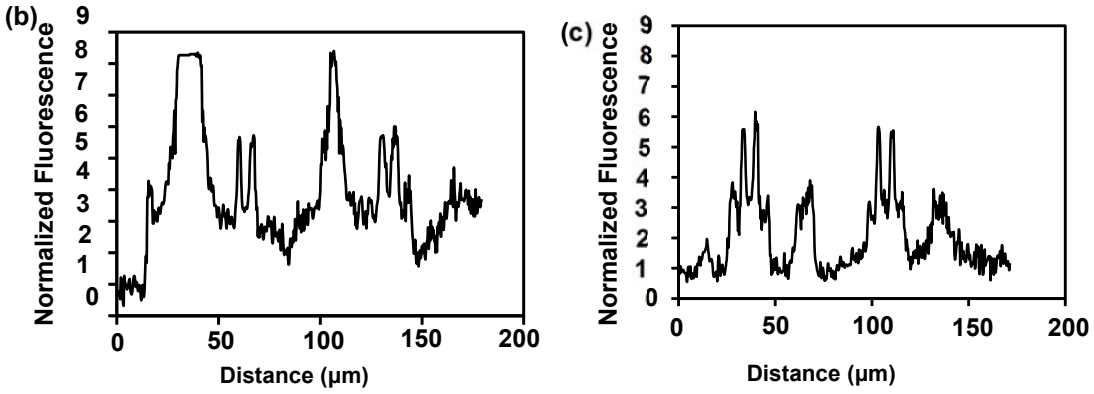


Figure S11. Fluorescence microscopy image (Zeiss Axiovert-200, λ_{ex} = 562 nm, λ_{em} = 624 nm) with printing condition that [DMPA]/[**1**] = 0.1 in DMF; light intensity 42.74 mW / cm^2 ; 365 nm UV light; exposure time 420 s; Z extend height with －9 μm. (b) Intensity profile of spot (1,1) and (0,1) in the inset. (c) Intensity profile of spot (-1,0) and (0,0) in the inset.

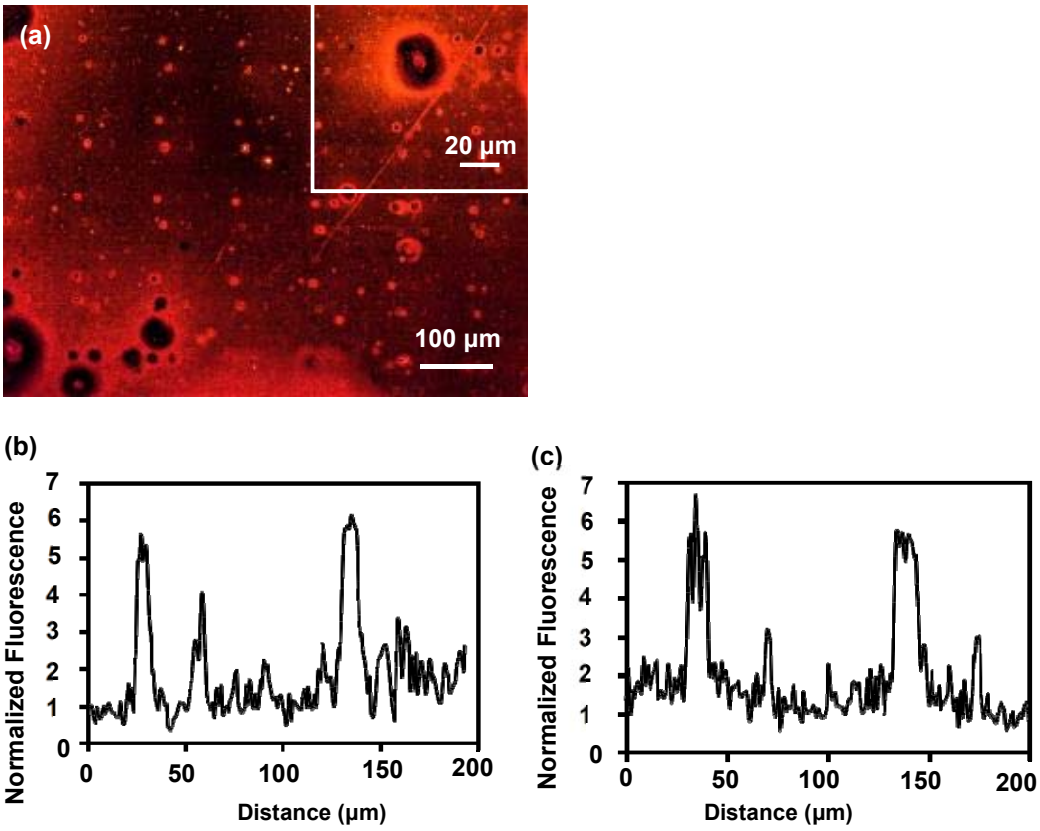


Figure S12. (a) Fluorescence microscopy image (Zeiss Axiovert-200, λ_{ex} = 562 nm, λ_{em} = 624 nm) with printing condition that [DMPA]/[**1**] = 0.1 in DMF; light intensity 42.74 mW/cm^2 ; 365 nm UV light with exposure time 480 s; Z extend height with －9 μm. (b) Intensity profile of spot (1,1) and (0,1) in the inset. (c) Intensity profile of spot (-1,0) and (0,0) in the inset.

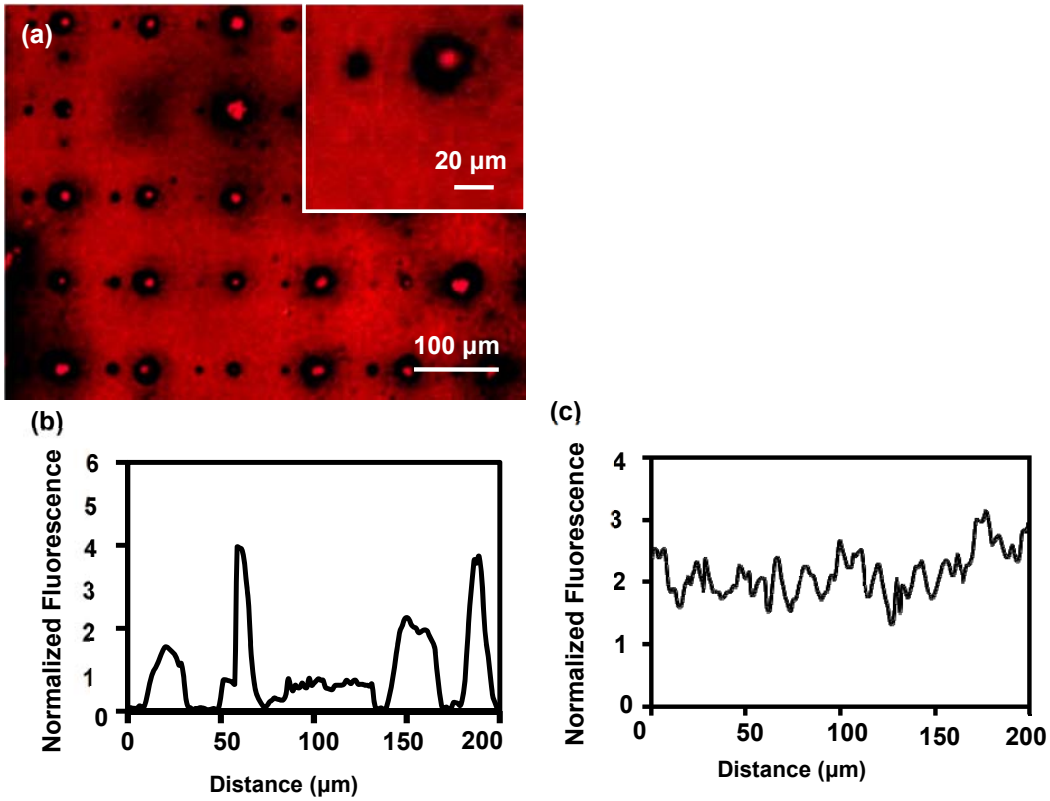
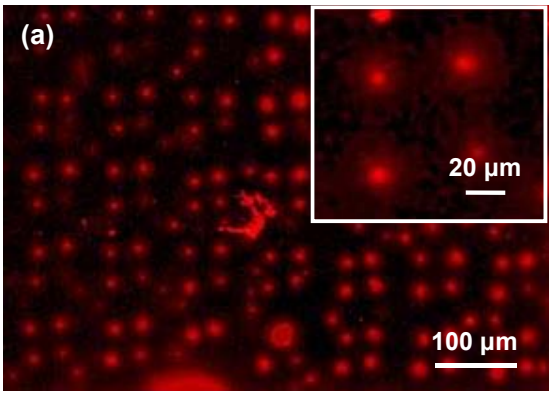


Figure S13. (a) Fluorescence microscopy image (Zeiss Axiovert-200, λ_{ex} = 562 nm, λ_{em} = 624 nm) with printing condition that [DMPA]/[**1**] = 0.1 in DMF; light intensity 42.74 mW/cm^2 ; 365 nm UV light; exposure time 540 s; Z extend height with －9 μm. (b) Intensity profile of spot (1,1) and (0,1) in the inset. (c) Intensity profile of spot (-1,0) and (0,0) in the inset.



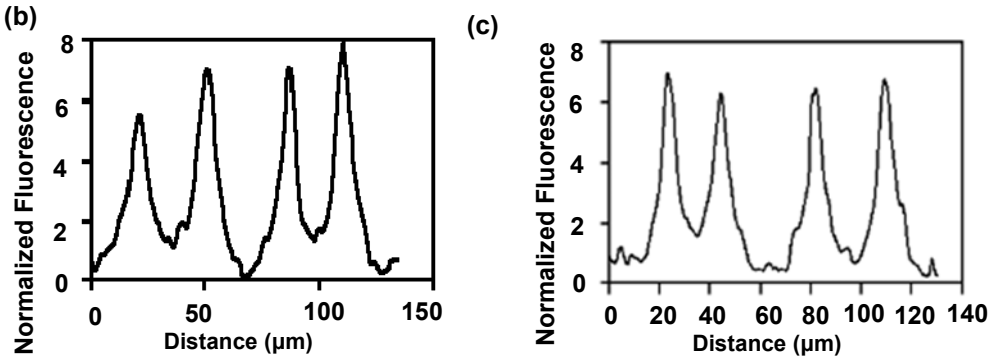


Figure S14. (a) Fluorescence microscopy image (Zeiss Axiovert-200, λ_{ex} = 562 nm, λ_{em} = 624 nm) with printing condition that [DMPA]/[**1**] = 0.1 in DMF; light intensity 42.74 mW/cm^2 ; 365 nm UV light; exposure time 480 s; Z extend height with -9 μm. (b) Intensity profile of spot (1,1) and (0,1) in the inset. (c) Intensity profile of spot (-1,0) and (0,0) in the inset.

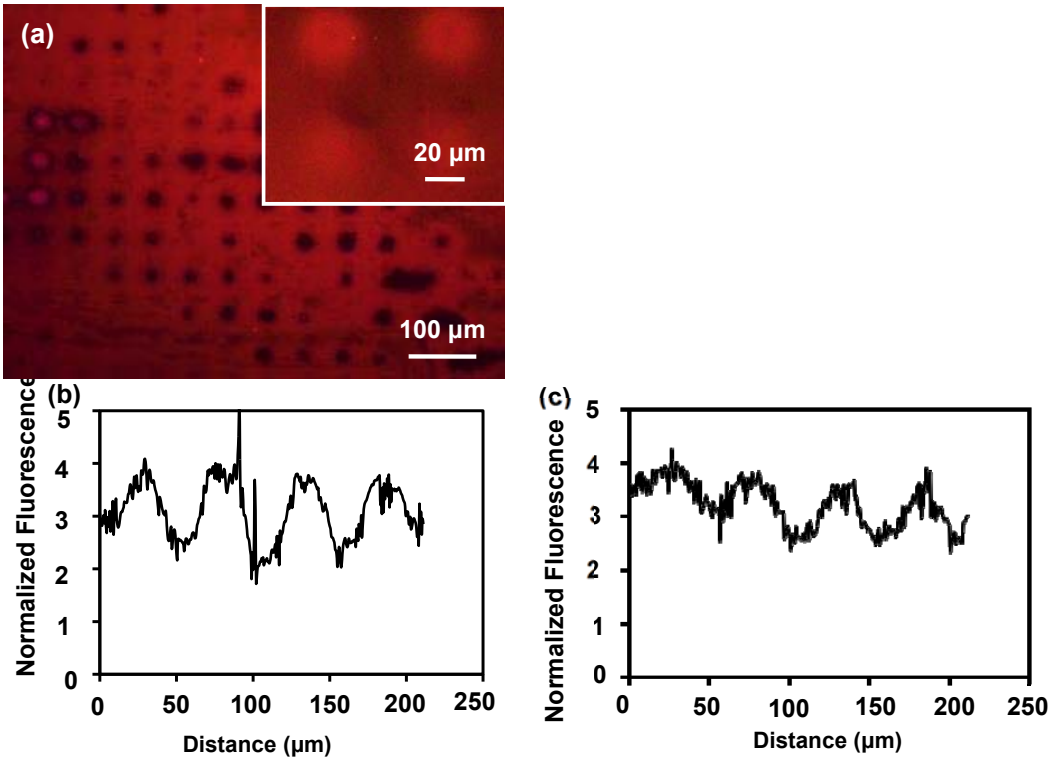


Figure S15. (a) Fluorescence microscopy image (Zeiss Axiovert-200, λ_{ex} = 562 nm, λ_{em} = 624 nm) with printing condition that [DMPA]/[**1**] = 0.1 in DMF; light intensity 42.74 mW/cm^2 ; 365 nm UV light; exposure time 540 s; Z extend height with -9 μm. (b) Intensity profile of spot (1,1) and (0,1) in the inset. (c) Intensity profile of spot (-1,0) and (0,0) in the inset.

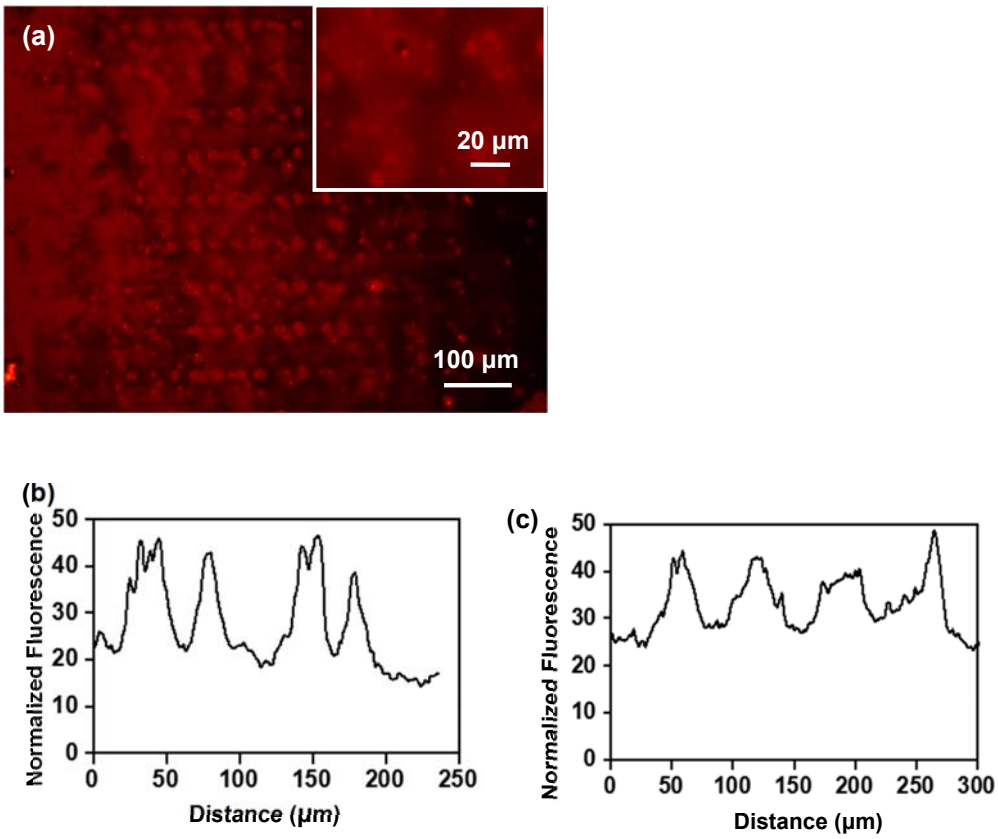


Figure S16. (a) Fluorescence microscopy image (Zeiss Axiovert-200, λ_{ex} = 562 nm, λ_{em} = 624 nm) with printing condition that [DMPA]/[**1**] = 0.1 in DMF; light intensity 42.74 mW/cm^2 ; 365 nm UV light with exposure time 660 s; Z extend height －9 μm. (b) Intensity profile of spot (1,1) and (0,1) in the inset. (c) Intensity profile of spot (-1,0) and (0,0) in the inset.

9. Multi-spot multi-color printing within photochemical reactor.

General methods. Massively parallel elastomeric tip array preparation and procedures for printing within the microfluidic photochemical nanoreactor were the same as described for dynamic multi-spot printing described in section **S8**. [**2**] (DMPA (0.03 mg 0.117 mM), **2** (0.46 mg 1.20 mM), 1 ml DMF) and [**3**] (DMPA (0.03 mg 0.117 mM), **3** (0.25 mg 1.20 mM), 1 ml DMF) ink solutions were prepared respectively for multi-color printing. Defined the coordination of 1 × 2 dot array with spot 1 (-35,0) μm and 2 (0, 0) μm and printed with ink **2** for spot **1** , ink **3** for spot **2**. 1 × 2 dot array weres printed by bringing the tip array into contact with the thiol-terminated glass surface

with exposure time 540 s for spot 1 and spot 2. UV-Vis spectroscopy described in S1 show that ink [**2**] have a emission wavelength between 500-670 nm and ink [**3**] have a emission wavelength between 400- 600 nm. Based on the overlap of emission, spot 1 can only be observed under 530-620 nm barrier filter but spot 2 can be observed under both 530-620 nm and 400-600 nm filter. Spot 1 was shown in Figure **S17(a)** and spot 2 was shown in **S17(b)**.

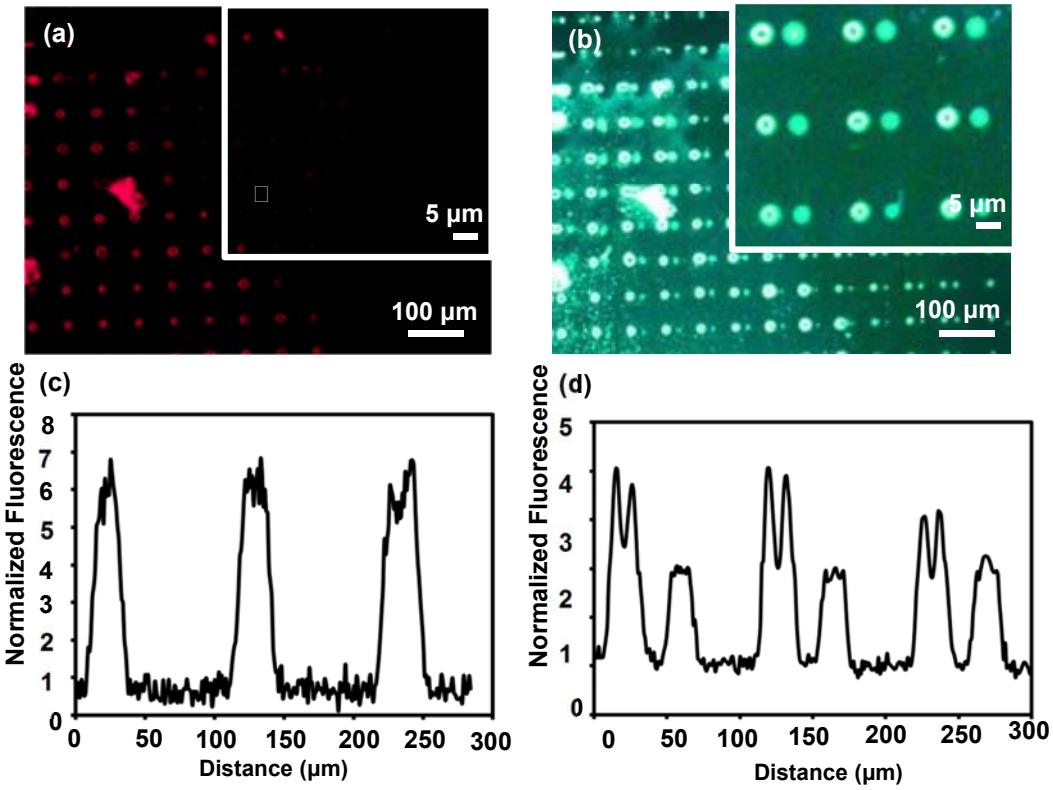


Figure S17. (a) Fluorescence microscopy image (Zeiss Axiovert-200, X 10, λ_{ex} = 522 nm, λ_{em} = 572 nm) of spot 1 (−35, 0) with printing condition that [DMPA]/[**2**] = 0.1; light intensity 42.74 mW/cm^2 ; 365 nm UV light with exposure time 540 s; Z extend height −9 μm. (b) Fluorescence microscopy image (Zeiss Axiovert-200, λ_{ex} = 354 nm, λ_{em} = 440 nm) of spot 1 (-35, 0) and 2 (0,0) with printing condition that [DMPA]/[**3**] = 0.1; light intensity 42.74 mW/cm^2 ; 365 nm UV light with exposure time 540 s; Z extend height −9 μm. (c) Intensity profile of spot in the inset of (a). (d) Intensity profile of spot in the inset of (b).

10. Atomic Force Microscopy for Multiple Spots

General methods. 1 was patterned onto the thiol-terminated glass surface by massively parallel flow- through photochemical nanoreactor. A 2 × 2 pattern was printed with condition that [DMPA]/[**2**] = 0.1; light intensity 42.74 mW/cm^2 ; Z extension －9 μm; 365 nm UV light with varying exposure time 300, 420, 480s, 540s for spot 1, 2, 3, 4. AFM characterization of the height profile of the features on the surface patterned with **1** after washing was performed on a Bruker Dimension Icon with an NCHR tip (NanoWorld, force constant / 42 Nm^{-1}). AFM data analysis was performed using XEI (Park Systems Corp.) analysis software.

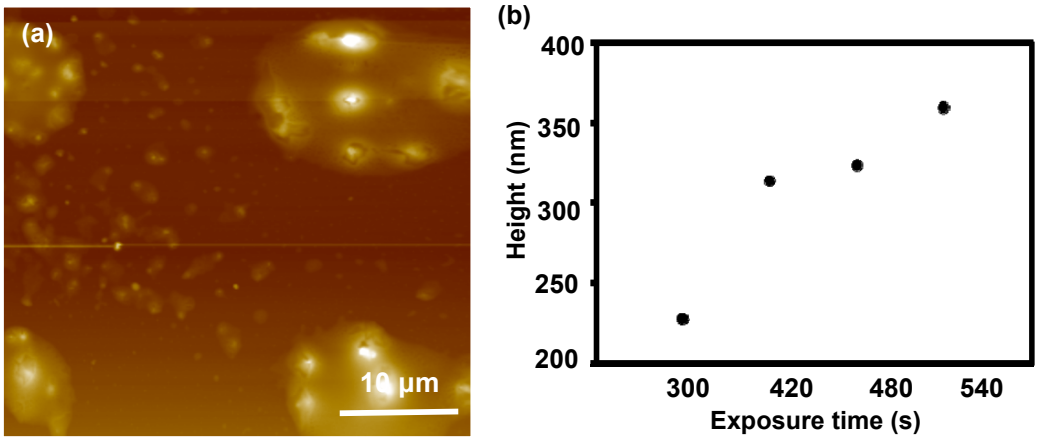


Figure S18. (a) AFM tapping mode image of a 2 × 2 pattern of **1** patterned onto the thiol-terminated glass slide with printing condition that [DMPA]/[**1**] = 0.1 in DMF; light intensity 42.74 mW/cm^2 ; 365 nm UV light; Z extend height －9 μm; dynamic printing and varying exposure time 300, 420, 480, 540s for spot 1,2,3,4. (b) Relationship between exposure time and polymer height.

12. References

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