Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Refractive index matched polymeric and preceramic resins for high resolution two photon lithography

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RIM resin formulations:

Table S1 Formulation mixture of refractive index matched (RIM)-resins using BPADA:PETA resin. RI was calculated using $RI_{xy}=1.49x+1.545y$ where x is mass fractions [mg PETA/ (mg BPADA + mg PETA)] and y is mass fractions [mg BPADA / (mg BPADA + mg PETA)].

ENTRY	BPADA (mg)	PETA (mg)	RI
1	115.4	882	1.4918
2	282.1	730.2	1.5019
3	439.6	564.6	1.512
4	540.5	501.4	1.517
5	591.8	414.6	1.5212
6	764.3	248.1	1.5317

Table S2 Effect of POSS:Thiophenol ratio on the RI of the preceramic photoresist using DBU (0.1 ml). The RI was calculated using $RI_f=m_{AcrylPOSS}\ RI_{AcrylPOSS} + m_{Thiophenol}\ RI_{Thiophenol}$ where $m_{AcrylPOSS}$ is the volume fraction of AcrylPOSS [$mL_{AcrylPOSS}/(mL_{AcrylPOSS} + mL_{Thiophenol})$], $m_{Thiophenol}$ is the volume fraction of thiophenol [mL thiophenol/($mL_{AcrylPOSS} + mL_{Thiophenol}$)].

ENTRY	POSS (ml)	THIOPHENOL (ml)	MOLE FRACTION OF THIOLPHENOL	MEASURED RI	CALCULATED RI	VOLUME FRACTION OF THIOLPHENOL
1	1.667	0.2	1.960	1.5013	1.497	0.107
2	1.667	0.25	2.450	1.5163	1.4995	0.130
3	1.667	0.38	3.724	1.52	1.505	0.186
4	1.667	0.46	4.508	1.526	1.508	0.216
5	1.667	0.54	5.292	1.529	1.511	0.244
6	1.667	0.5	4.900	1.53	1.510	0.231
7	1.667	0.75	7.351	1.5348	1.518	0.310
8	1.667	1	9.801	1.57	1.525	0.375

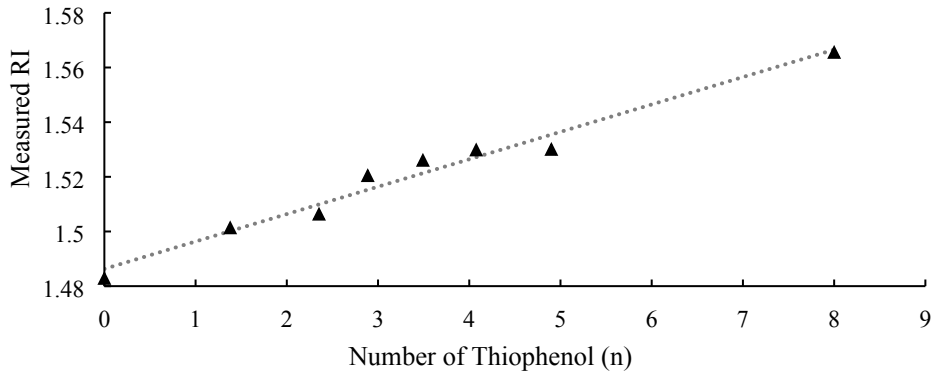

Figure S1 Change of the RI of the preceramic photoresist as a function of covalently bound thiophenol groups.

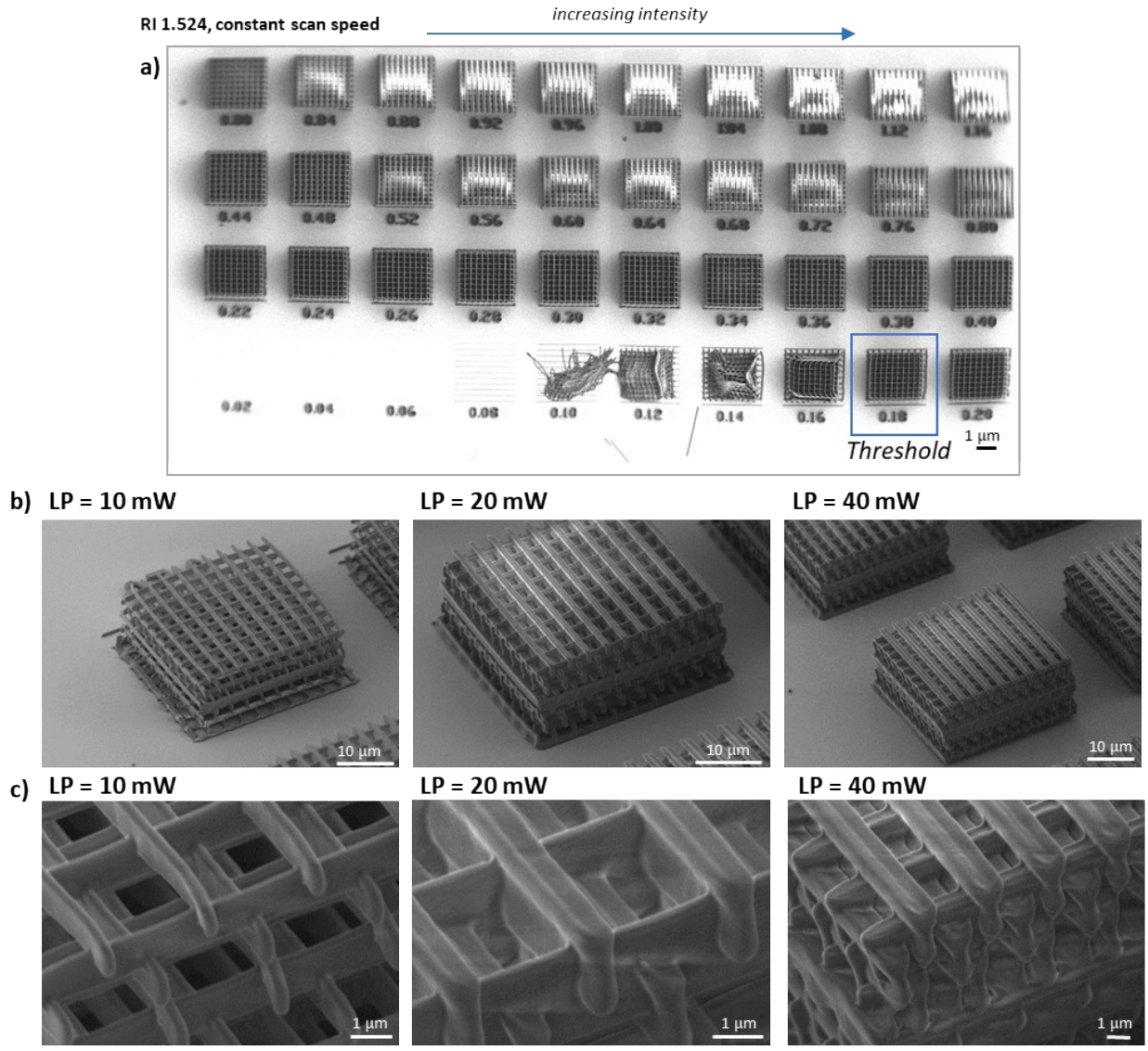

Figure S2 SEM of BPADA:PETA resin at 1.524 RI, a) effect of laser power (LP) on DLW-2PP single voxel logpile test structures printed with a 63x lens . Here, 'threshold' marks the freestanding logpile sample printed with the lowest laser intensity. b) SEM of printed structure beyond the threshold at 10, 20, 40 mW laser power. C) closeup of printed voxel showing shape deformity beyond threshold.

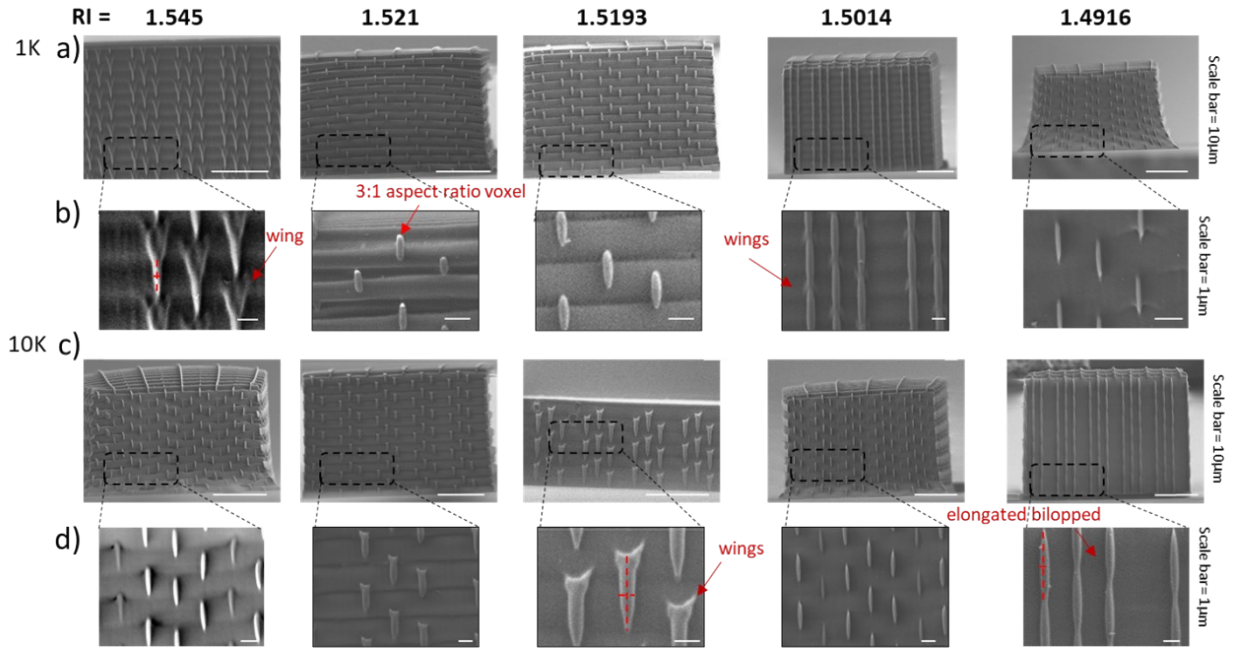

Figure S3 SEMs of BPADA:PETA resin test structures designed to show the effect of photoresist RI and laser intensity on voxel size and shape: a, b) laser intensity of 1K and c, d) laser power 10K (DLW-2PP system with 63x lens).

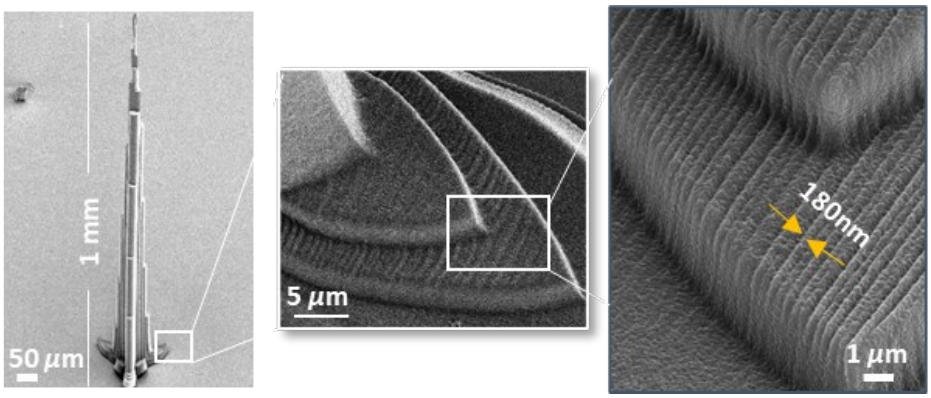

Figure S4 SEM of RIM-preceramic resin print of Burj Khalifa tower at 1mm height with 1.5um feature size using dip-in approach.

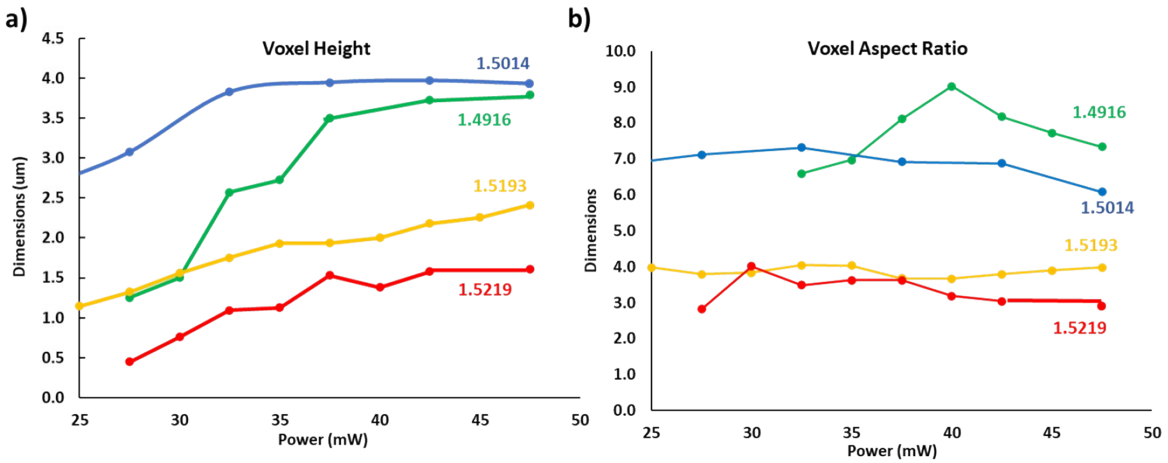

Figure S5 Effect of laser power on a) voxel height and b) voxel aspect ratio for photoresists with different RIs ranging from 1.4916 to 1.5219. SEM images of the voxels used for this measurement are shown in figure S3-d

Energy Dispersive X-Ray Analysis (EDS) – EDAX Element Detector

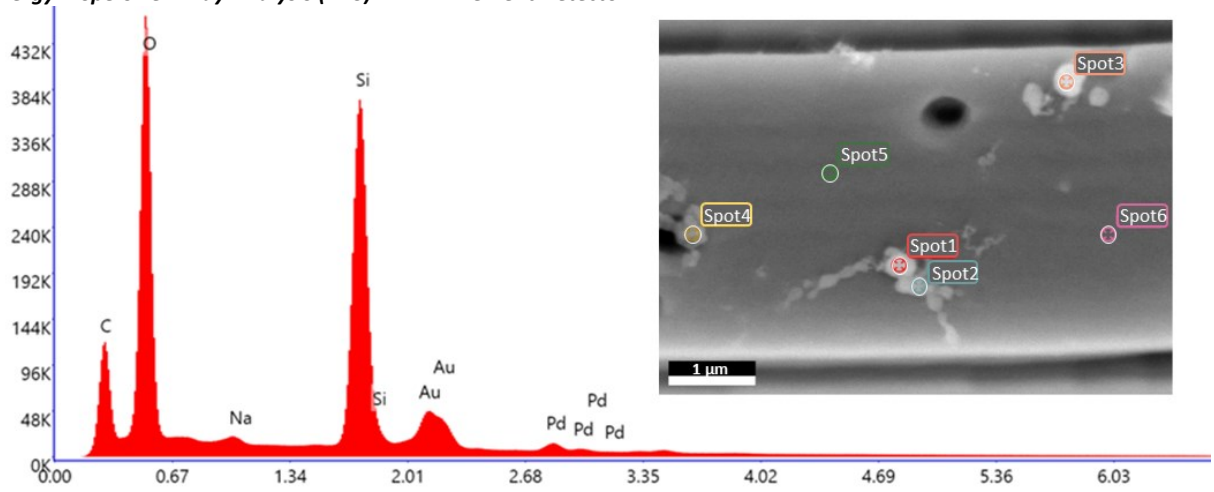

Figure S6 Representative EDS spectrum of a pyrolyzed SiOC sample coated with Au/Pd. The inset shows an SEM image of the sample used for the EDS analysis. Spots analyzed by EDS are marked by numbers and quantitative results are shown in Table S3. The Au and Pd EDS peaks in the EDS spectra can be attributed to the Au/Pd coating

Table S3 integrated EDS peaks of multiple spots on pyrolyzed ceramic printed nanostructure showing atomic % and wt.% of each C, O, Na, and Si.

	Atomic %				Weight %			
Element	Spot 1	Spot 4	Spot 5	Spot 6	Spot 1	Spot 4	Spot 5	Spot 6
C	24.87	22.10	23.69	23.76	15.88	13.47	14.46	14.45
O	43.47	39.89	38.00	37.30	36.96	32.39	30.90	30.21
Na	0.35	0.21	0.21	0.10	0.43	0.25	0.24	0.12
Si	31.30	37.80	38.10	38.84	46.72	53.89	54.36	55.22

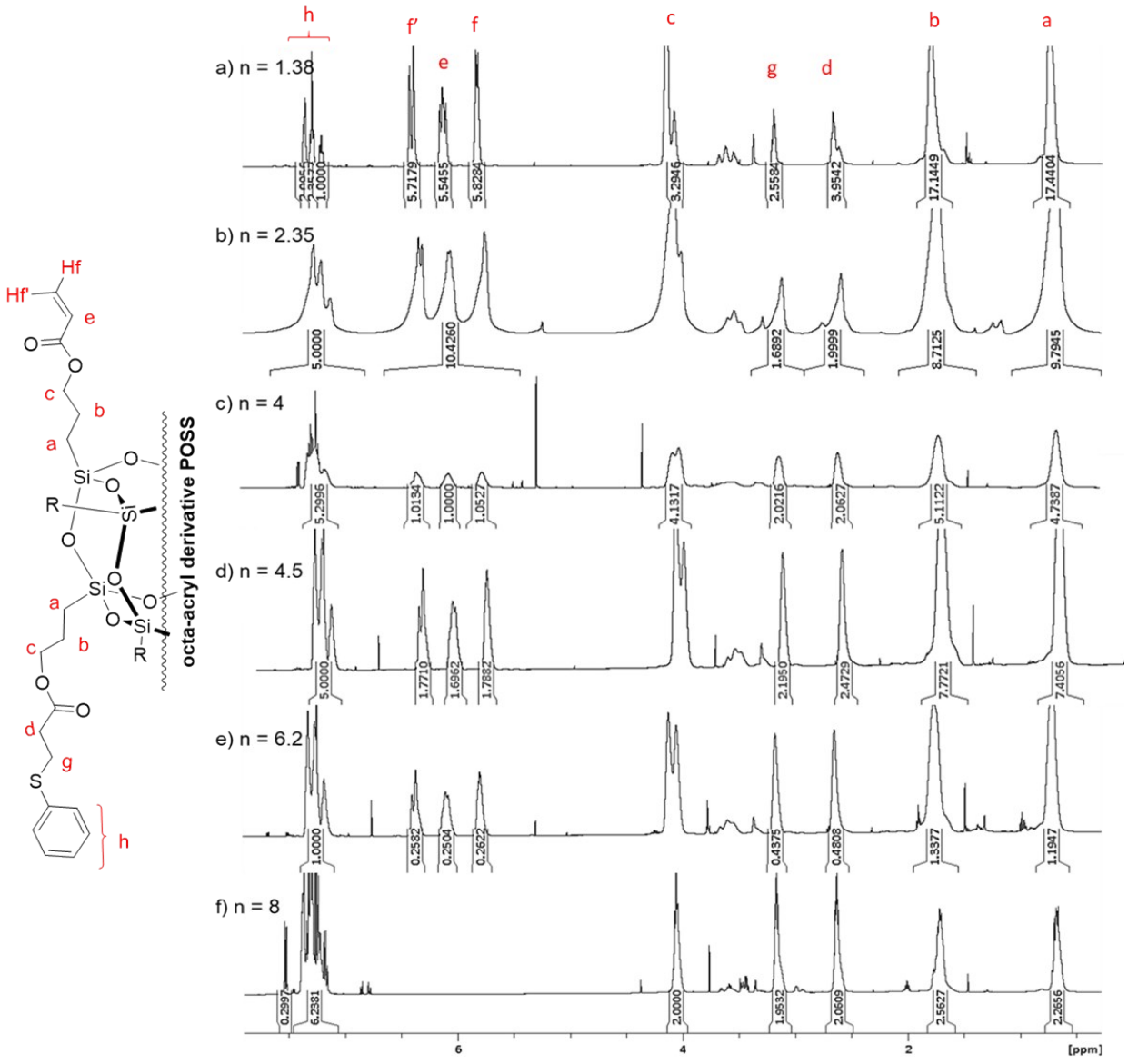

Figure S7 ^{1}H NMR in $CDCl_3$ of preceramic functionalized octa-acryl derivative POSS compounds with pendant n number of phenol thiol.