Electronic Supplementary Information

Simultaneous laser-induced synthesis and micro-patterning of a metal organic framework

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Experimental section

Sample preparation. The solution containing the precursors was prepared by dissolving 0.134 g of iron(III) acetylacetonate (Stream Chemical, Inc.) and 0.063 g of 1,3,5-benzenetricarboxylic acid (trimesic acid, Aldrich) in 1 ml of N,N-dimethylformamide (DMF, Daejung). The solution was stirred for 30 minutes at room temperature. Samples were prepared by placing two clean standard microscope cover slips (#0, 100 µm thick), one on top of the other, with a Parafilm™ tape as a spacer. The solution was inserted between the two cover slips by capillary forces.

Optical setup. The optical setup (illustrated in **Figure 1a**) consists of a CW laser (532 nm, MGL-N-532A-4W, CNI) that is relayed by a dichroic mirror to an objective lens of a microscope (Nikon ECLIPSE LV100ND). We used a 50× (TU Plan ELWD, 0.6 NA, Nikon) objective lens. Modulation of the laser was performed by electrical means – controlling the power delivered to the laser diode – using transistor-transistor-logic (TTL) modulation (part of the laser driver circuit). The square-wave signal for the TTL modulation was generated by a Siglent function generator (SDG 5162).

The laser power was set to 1.3 mW (unless stated otherwise) with a modulation of 20% duty cycle and a frequency of 1 kHz. The reported laser intensity was measured after the objective lens with a power meter (PM100, Thorlabs) while applying the modulation. A mechanical shutter (SH05, Thorlabs) was used for achieving the ring formations in **Figure 4b**. The microscope stage was computer-controlled with a velocity of 10 µm/s, and the experiments were recorded by a CMOS camera (DPCAM, DeltaPix). We note that the micro-patterning of MOFs is not limited to setups where the laser is directed from above the sample. We achieved almost identical results when micro-patterning was formed on the bottom cover slip, with another optical setup based on an inverted microscope (Nikon, Eclipse Ti-U) using a 532 nm CW laser (DPSS laser, 5-532-DPSS-0.5-LN, Verdi) modulated by an optical chopper (MC1F100, Thorlabs). For simplicity and clarity, we focus our report on the first setup discussed above based on an upright microscope.

Characterization methods. X-ray diffraction (XRD) measurements were obtained using a Rigaku SmartLab X-ray diffractometer with Cu-Kα radiation (λ = 1.5406 Å, 40 kV and 30 mA) utilizing parallel beam optics. The scanned 2θ range was 2–40° with a step size of 0.02° and rate of 0.5 °/min.

Micro Raman measurements were performed using a confocal Raman microscope with 532 nm laser excitation, a 100× objective, a 100 µm confocal pinhole, and a 600 groves/mm grating (LabRAM HR, Horiba Jobin Yvon Corporation). The laser power was 60 mW, and a neutral density filter of optical density 1 was inserted in the beam path to prevent optical damage to the sample. The acquisition time was 30 s per scanning interval (~500 cm^{-1}), with all measurements taken in air at room temperature. IR transmission measurements were performed using a Nicolet iS10 FTIR system.

The samples for XRD, Raman and FTIR were prepared by micro-patterning many individual lines of MOFs on a glass slide with minimal spacing in-between lines to form a ~500 µm × 2 cm sample with laser intensity of 10.6 mW.

SEM images were obtained using a Quanta FEG 250 System with a built-in energy dispersive X-ray spectroscopy (EDS) system. HRSEM images were obtain by a FEI, Magellan 400L system. The preparation of samples imaging the cross-section of the micro-patterned MOF (**Figure 4c & 4d**)

was performed by breaking the cover slip with the deposited material at selected locations, determined by scratching with a diamond knife (without physically touching the deposits). HRTEM images were obtained using a JEOL-2100 operated at 200 KeV, and the elemental analysis was conducted by Energy Dispersive X-ray Spectroscopy (EDS). For HRTEM measurements, the solution was prepared as described above, followed by diluting with DMF and filtration with a hydrophobic 0.22 μm PTFE syringe filter. A droplet (~100 μL) was positioned on a glass slide and held in place by capillary forces. After five minutes of laser illumination (at 10.6 mW), a TEM grid (Lacey carbon, 300 mesh copper grid, Ted Pella Inc.) was placed in contact with the bottom part of the droplet (at the solution/air interface) where the concentration of the formed nano-MOFs is maximal due to gravity. The TEM grid was washed with DMF and ethanol.

The measurements of the width and height of the deposits at different intensities were performed using an optical profilometer (LEXT OLS4100, Olympus). Each line was automatically averaged over >100 points. To obtain the data presented in **Figure 5**, for each reported intensity, three separate experiments were performed. In each experiment, five lines were deposited, thus each data point includes 15 individual measurements.

Author Contributions

Conceptualization, N.A, A.K., and H.S.; Investigation, N.A., E.G., O.K., O.F., I.P. and G.C.; Methodology, N.A., I.P., G.C., I.H. and H.S.; Formal analysis, N.A., I.P., G.C., I.H. and H.S. ; Funding acquisition, H.S.; Resources, H.S.; Supervision, I.H. & H.S.; Validation, N.A., E.E., S.P., I.H. and H.S.; Visualization, E.E. and N.A.; Writing – original draft, N.A., E.G. and H.S.; Writing – review & editing, N.A., E.G., I.P., G.C.,S.P., I.H. and H.S.;

Figure S1:

HRTEM images show that the laser indeed produces nano-MOFs (Fig. 4a and Fig. S1a-c). In addition, SADP measurements indicate that the fabricated nano-MOFs are amorphous (Fig.S1d). In addition, EDS spectrum (Fig.S1e) verifies the presence of iron, thus dismissing the option that only the BTC ligand is present.

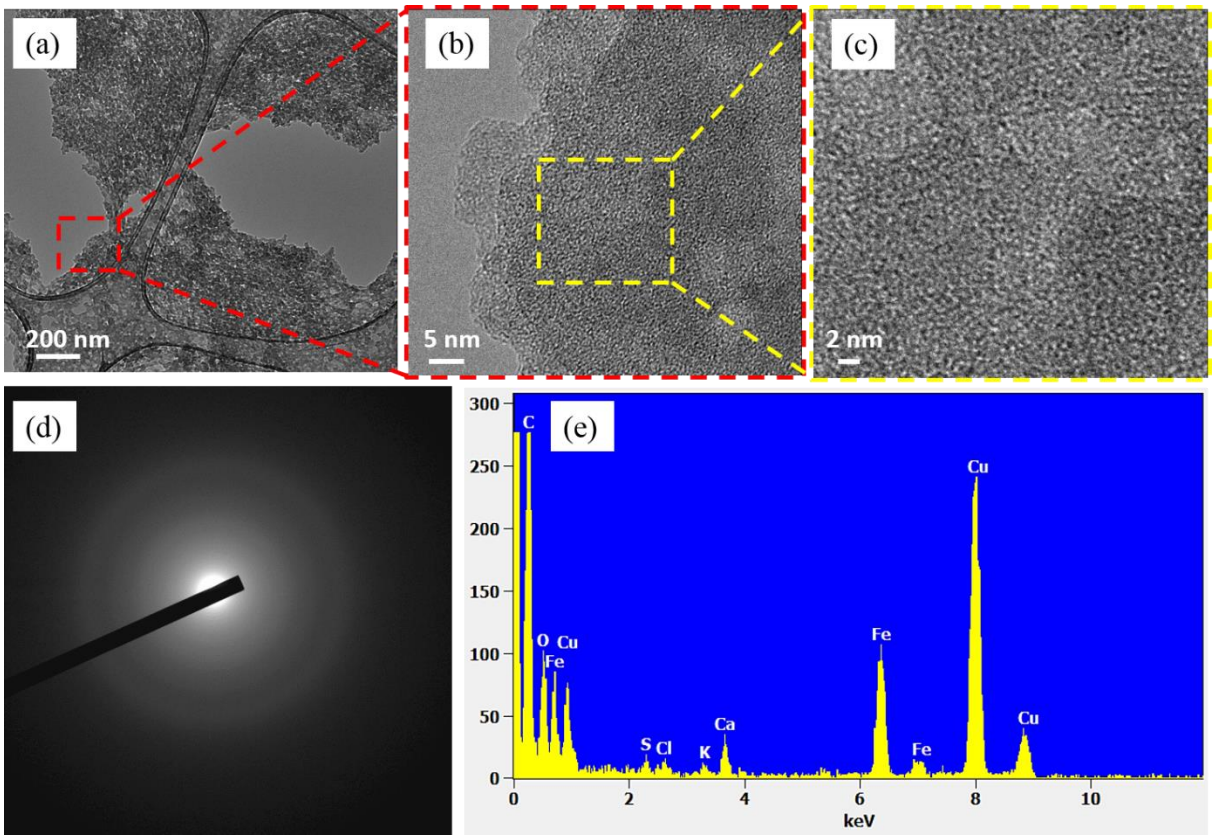

Fig. S1: (a-c) HRTEM images showing the formation of nano-MOFs. (d) SADP measurements of the iron-based MOF. (e) EDS spectrum verifying the presence of iron and carbon.

Video SV1: laser synthesis of nano-MOFs.

Formation of nano-MOFs inside a droplet – a 1.3 mW laser beam was focused inside a droplet with MOF precursors, situated more than 50 µm away from the substrate. The solution immediately turned cloudy around the focal point.

Video SV2: micro-patterning by M-LIMBT.

Micro-pattern formation - by moving the microscope stage at a velocity of 10 µm/s along a predetermined path while the 1.3 mW laser beam was focused at the substrate/solution interface, continuous patterns of a MOF is formed. A micro-bubble is evident at the location of the laser focal point.