Electronic Supporting Information

Printing of Covalent Organic Frameworks Using Multi-Material In-air Coalescence Inkjet Printing Technique

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Experimental Section

1.1 Materials

For the synthesis of crystalline COF, 1,3,5-tris-(4-aminophenyl) benzene (TAPB), 1,3,5-benzenetricarbaldehyde (BTCA), acetic acid (50%, w/w in water) and tetrahydrofuran (THF) were used. TAPB (4496AL, CAS 118727-34-7) was purchased from AK Scientific, BTCA (753491, CAS 3163-76-6), acetic acid (A6283, CAS 64-19-7) and THF (178810, CAS 109-99-9) were obtained from Sigma-Aldrich. All chemicals were used as received without any treatment.

1.2 Sample preparation

In the typical ink preparation, 21.7 mg of TAPB was dissolved in 1.55 ml of glacial acetic acid (TAPB ink) and 10 mg of BTCA was dissolved in 1.55 ml of glacial acetic acid (BTCA ink). COF samples were prepared by two approaches. Drop-cast COF: The TAPB and BTCA inks were added directly onto glass substrates using pipettes one after the other. Printed COF: The TAPB and BTCA inks were loaded into reservoirs connected to piezoelectric printheads (MJ-ATP-01, 60 μm diameter orifice, MicroFab Technologies), respectively. The ejection of droplets was controlled by a driver unit (JetDrive III CT-MC3-4, MicroFab Technologies, Plano, TX, USA). A pneumatic controller (CT-PT-4, MicroFab Technologies) and a rotary vane pump RZ 6 (VACUUBRAND, Germany) were used to control static pressure for the drop-on-demand operation. Droplet images were acquired using a LED, Supereyes B008 USB portable digital microscope, and Basler ace acA640-120gm camera. All the images were processed and analyzed using ImageJ software. COF structures were designed via production of a G-code that controls the XY motion of the high resolution 2D motorized stage (Suruga Seiki PG650-L05AG-E1) with a microcontroller (Arduino Mega 2560). Droplets were ejected from both nozzles and coalesced in-air to initialize the polymerization of COF before reaching the substrates. In both cases, the obtained COF was repeatedly washed with THF and dried under vacuum at 150 °C for 24 h to yield crystalline COF. Unless stated otherwise, all the samples were inkjet printed onto 10 mm × 10 mm glass substrates that had been cleaned with a detergent solution and then sonicated in acetone and isopropyl alcohol for 10 min each. The glass substrates were pretreated in UV/O_3 plasma for 15 min, if necessary

1.3 Characterization of Printed and Drop-cast COF

Rheological properties of TAPB and BTCA were measured using a rheometer (Brookfields LVDV3T) under couette flow-conditions. The surface tension of the ink was measured using a torsion balance, model "OS" (White Electrical Instrument Co. Ltd.). Optical microscopy image was taken using a CETI TRITON II materials microscope. Thickness measurement was determined using a Bruker Dektak XT. XRD pattern was obtained using Ultima IV Rigaku XRD system with Cu-Kα radiation (λ=1.54 Å) operated at 40 kV and 30 mA at room temperature. The XRD spectra were measured in the 2θ angular region between 4^{O} and 30^{O} with a step size of 0.02^{O}. FTIR measurement was done on an FTIR spectrometer (Bruker, Vertex 70, US). The FTIR spectra were acquired in the range of 400−4000 with a resolution of 4 cm^{-1} and averaged over 32 scans. SEM images were obtained using an analytical field emission SEM (Hitachi SU-70, Japan) operated at 10 kV. Samples were Pt-sputtered using Hitachi E -1045 ion sputter with Pt target and a current of 25 mA for 30 s. Platinum layer is 2-3 nm. Nitrogen adsorption isotherms were performed using Micromeritics 3Flex at 77K. Before measurement, the samples were degassed in vacuum at 150 °C for more than 12 h. AFM images were obtained in tapping mode using a silicon probe with a tip radius <10 nm, f ≈ 300 kHz, and k = 40 N m^{-1} (BudgetSensors) under Asylum Research Cypher ES AFM (Oxford Instrument). TGA was carried out using Netzsch STA 449 F5

Jupiter analyzer on alumina pan from room temperature to 1000 °C with a heating rate of 10 K min^{-1} under argon atmosphere.

Table S1. Fluidic properties of TAPB and BTCA inks.

Ink	Concentration ($mmol\ mL^{-1}$)	Density ($kg\ m^{-3}$)	Viscosity (mPa.s)	Surface tension ($mN\ m^{-1}$)	Ognesorge number, Z
TAPB	0.04 M	1086	1.21	37	40.58
BTCA	0.04 M	1098	1.25	38	40.03

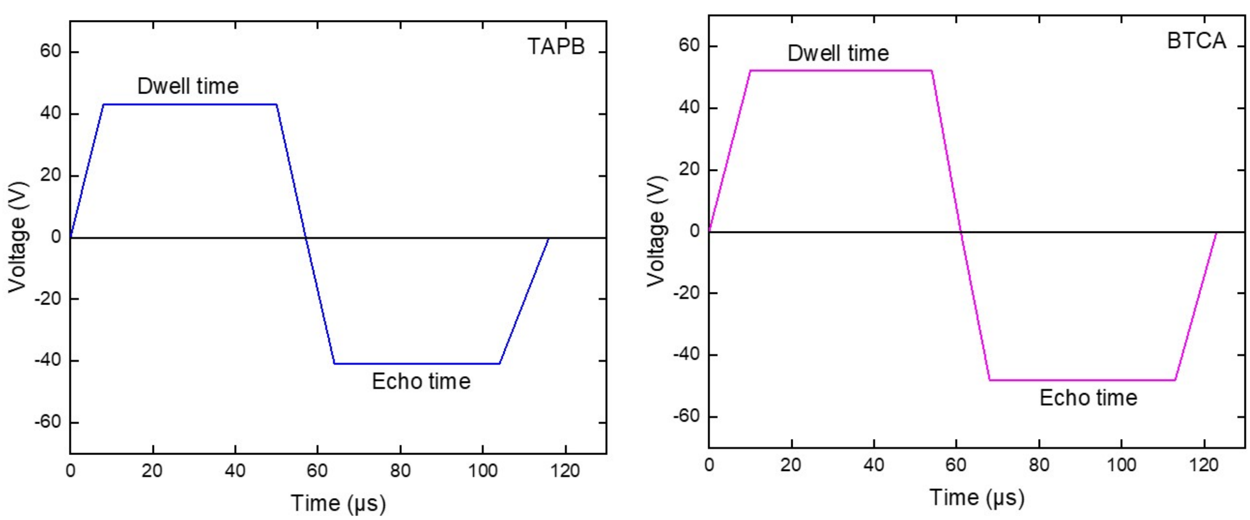

Fig. S1 Jetting parameter of TAPB and BTCA inks.

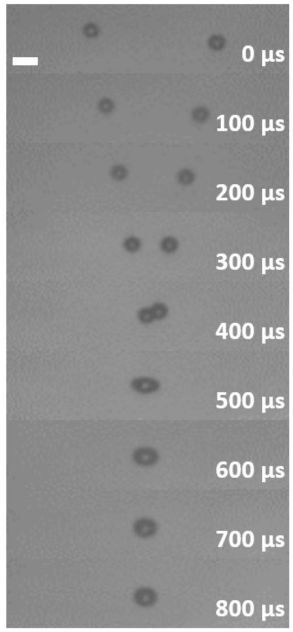

Fig. S2 Droplet coalescence of BTCA and TAPB droplet. BTCA droplet travels at 1.55 m/s, TAPB travels at 1.67 m/s and the coalesce droplet travels at 1.31 m/s. The diameter of nozzle is 60 µm and the jetting frequency 300 Hz. Scale 100 µm.

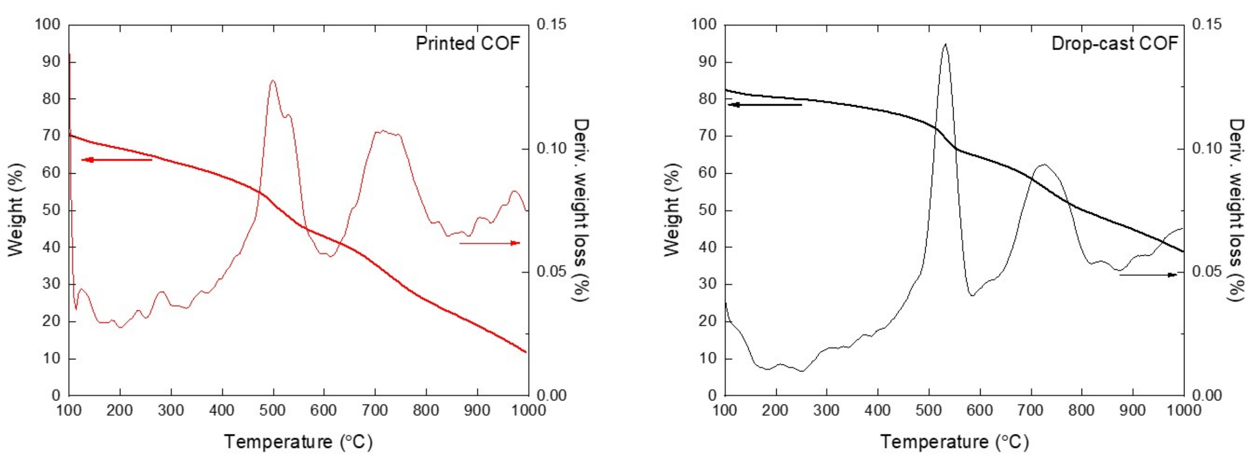

Fig. S3 TGA and derivative weight loss of printed and drop-cast COF.

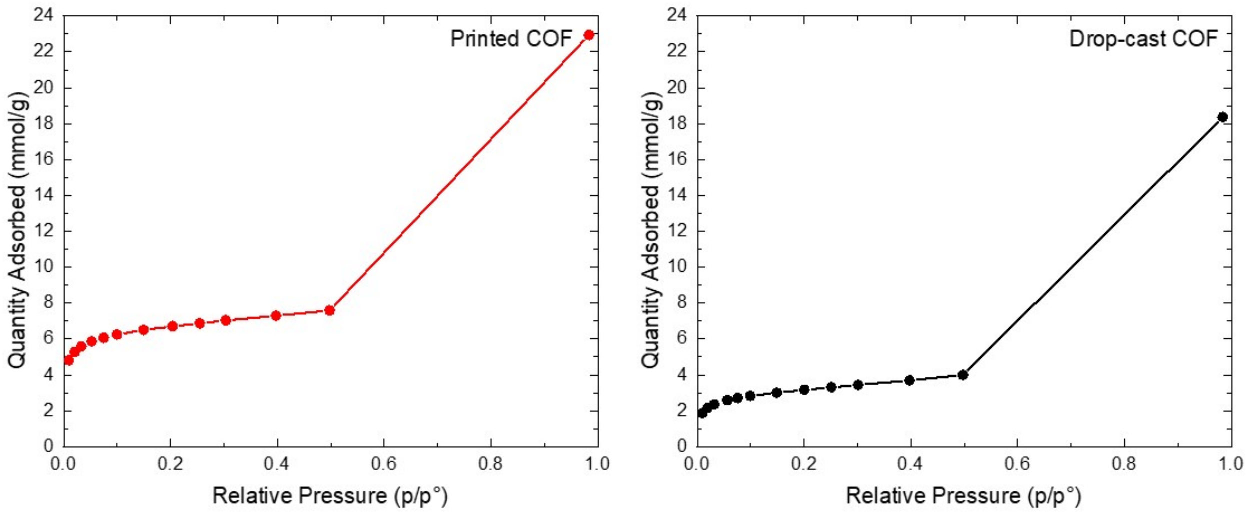

Fig. S4 Nitrogen adsorption isotherm at 77 K of printed and drop-cast COF.

Video Supporting

Movie S1. Droplet coalescence (4x speed)

Movie S2. Thin film formation on glass substrate (8x speed)

Movie S3. Pillar formation on glass substrate (8x speed)