Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis of Stack Plate Covalent Organic Framework Nanotubes using Self-Assembled Acid as a Soft Template

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1. Experimental Section

1.1. Materials

1,3,5-triformylbenzene, *p*-phenylenediamine, trimesic acid, 1,4-dioxane, acetic acid, tetrahydrofuran and acetone were supplied by Sigma-Aldrich company. Oleic acid, silicone oil, n-dodecane, squalene and Sudan III were purchased from Aladdin Chemical company. Deionized water was obtained from a Millipore system. All chemicals were analytical grade and used as received without further purification.

1.2. Synthetic procedures

COF-LZU1: 160 mg of 1,3,5-triformylbenzene were dissolved in 10 ml 1,4-dioxane in a 50 ml glass bottle. The solution was subjected to ultrasonic for 10 min and stirring for 10 min. Then, 160 mg of *p*-phenylenediamine were added to the solution and stirred for another 10 min. Next, 0.2 ml of 3 M acetic acid aqueous solution were added with continuous stirring for 30 min. The obtained solution with yellow precipitates was sealed with the cap and stood for 3 days at ambient conditions. The produced yellow precipitates were separated by centrifugation and then washed by tetrahydrofuran and acetone 3 times, respectively. After drying at 60 ^{o}C overnight, the obtained yellow powders were subjected to solvent exchange with methanol 3 times at 80 ^{o}C. The resulting COF-LZU1 was finally collected after drying at 120 ^{o}C overnight.

COF-LZU1-NT: 80 mg of TFA and 40 mg of TMA were firstly dissolved in 10 ml dioxane with a 50 ml glass bottle. The solution was subjected to ultrasonic for 10 min and stirred for 10 min to get a clear solution. Then, 160 mg PDA was added to the solution and stirred for another 10 min. Next, 0.2 ml of 3 M acetic acid solution were added to the solution with continuous stirring for 24 h. The obtained solution with green precipitates was sealed with the caps and stood for 2 days at ambient conditions. The produced green precipitates were separated by centrifugation, followed by the washing of tetrahydrofuran and acetone 3 times. After drying at 60 ^{o}C overnight, the obtained green powders were treated by the solvent-exchange with methanol 3 times at 80 ^{o}C. Finally, the dark-yellow-like COF-LZU1-NT was obtained after drying at 120 ^{o}C overnight.

1.3. Characterizations

The X-ray diffraction (XRD) was recorded on a PANalytical Empyrean X-ray diffractometer in Bragg-Brentano configuration with the 0.02° step size and 1 s step time, during which the Cu Kα radiation (40 kV and 30 mA) was used as the X-ray source. The crystalline phases were identified by comparing the diffraction patterns with those of the standard powder XRD files (JCPDS).

The surface areas and pore size were measured by N_2 adsorption-desorption isotherms (Micromeritics, physisorption analyzer, ASAP 2020). Before the measurements, the samples were outgassed at 393 K for 6 h. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method. The total pore volume was determined from the amount of adsorbed nitrogen under a relative pressure of about 0.99. The pore size distributions were calculated from nitrogen isotherms using the nonlocal density functional theory (NLDFT) method.

The scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) were carried out on Zeiss Ultra-55 microscope operated at 2 kV.

For transmission electron microscopy (TEM) analysis, the scanning mode was performed on a JEOL 2100 FEG S/TEM microscope with an operating voltage of 200 kV and equipped with a spherical aberration probe corrector. Before analysis, the samples were dispersed in ethanol and deposited on a holey carbon-coated TEM grid. The Fourier transform infrared (FTIR) spectra were recorded using a Thermo Fisher Scientific Nicolet 6700 FTIR (32 scans at a resolution of 4 cm^{-1}) equipped with a mercury cadmium telluride (MCT) detector.

The solid-state ^{1}H, ^{13}C, and ^{15}N Nuclear Magnetic Resonance (NMR) spectra were measured at 9.4 T on a Bruker Avance 400 spectrometer with a 4 mm probe. A double air-bearing probe and a zirconium oxide rotor were utilized. The acquisition was performed with a standard CP pulse sequence. The spinning speed was 12.5 kHz for ^{13}C and 5 kHz for ^{15}N CPMAS (Cross Polarization Magic Angle Spinning) and 12.5 kHz for ^{1}H MAS

The thermal gravimetric (TG) analysis of COFs was performed on a Simultaneous Thermal Analyzer (STA) 8000 in a temperature range of 100 to 600 °C under a nitrogen atmosphere with a heating rate of 10 °C/min.

1.4. Adsorption of oil

A certain amount of COFs materials (m_1) were placed on a glass plate. Then, the oil selected from oleic acid, silicone oil, *n*-dodecane, squalene, cooking oil was dropwise added using the micro-syringe, thoroughly mixing the oil and COFs by rubbing with the spatula. Until a stiff paste was produced, the COFs with oils were weighed. The test was repeated 3 times and the weight measurements were averaged (m_2). The adsorption capacity was calculated according to the following equation:

$$\text{Adsorption capacity=} \frac{m_2 - m_1}{m_1} \qquad (1)$$

The oil-in-water emulsions separation test was performed by a filtration process according to the reference [1]. The homogeneous oil-in-water emulsions are prepared by mixing 9.9 ml of deionized water, 0.1 ml of oleic acid, 0.3 g of hexadecyl trimethyl ammonium bromide, and 5 mg of Sudan III and ultrasonicated for 10 min. Then, 20 mg of the prepared COF powder were filled into the head of a needle filter. The oil-in-water emulsion was fed through the filter by a plastic syringe under constant pressure.

References

1. L. Chen, J. Du, W. Zhou, H. Shen, L. Tan, C. Zhou and L. Dong, *Chem. Asian. J.*, 2020, **15**, 3421-3427.

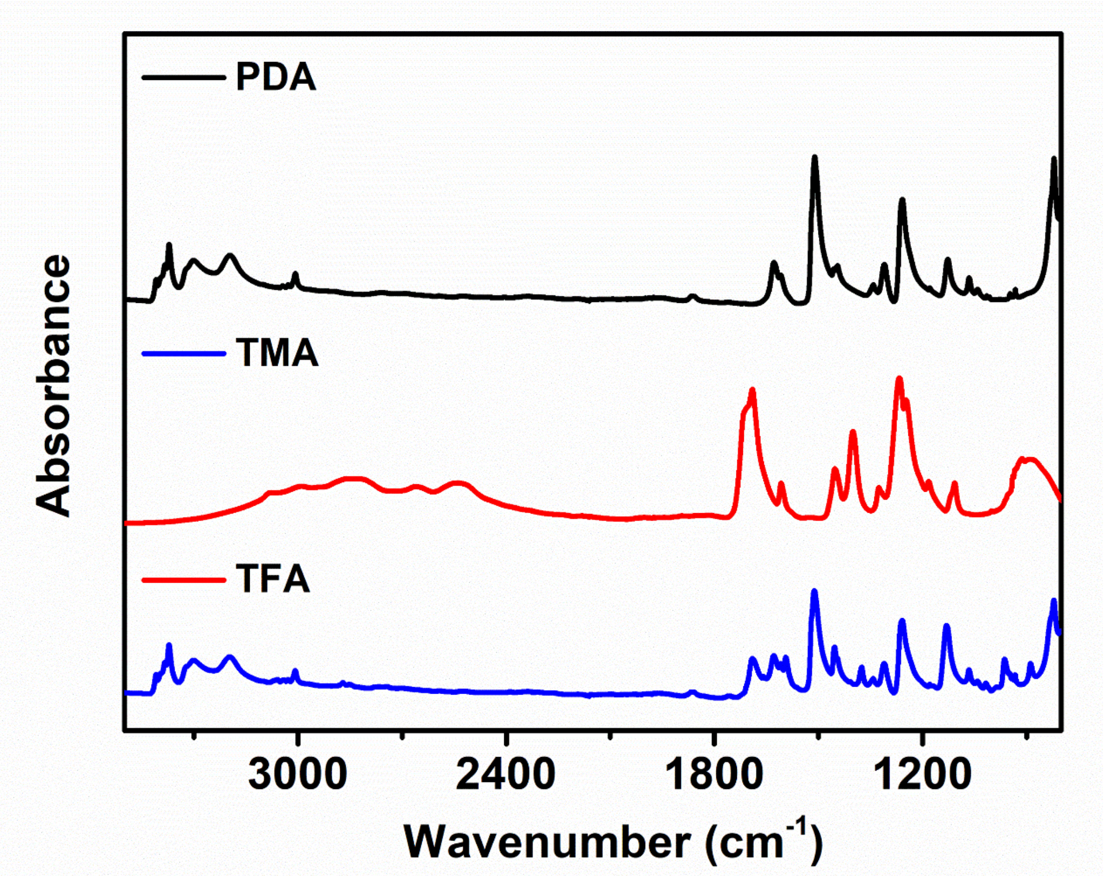

Figure S1. FTIR analysis of the precursor of PDA, TMA and TFA.

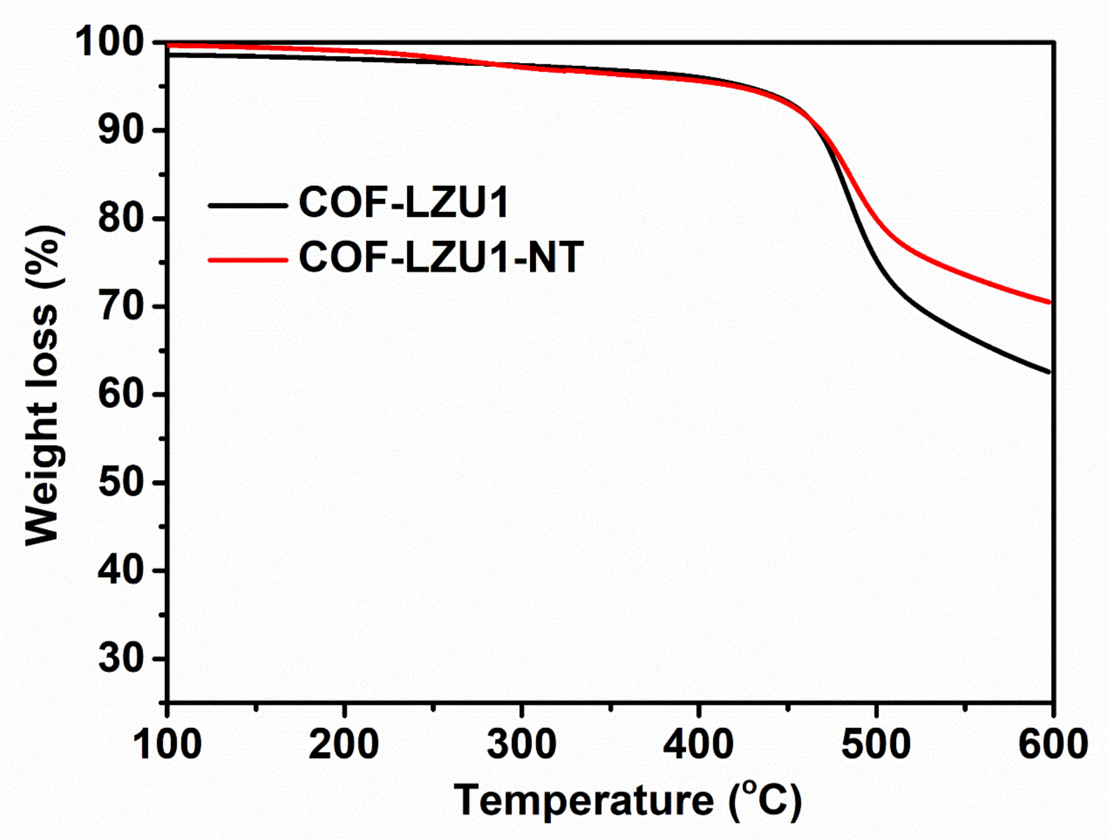

Figure S2. TG analysis of the COF-LZU1 and COF-LZU1-NT.

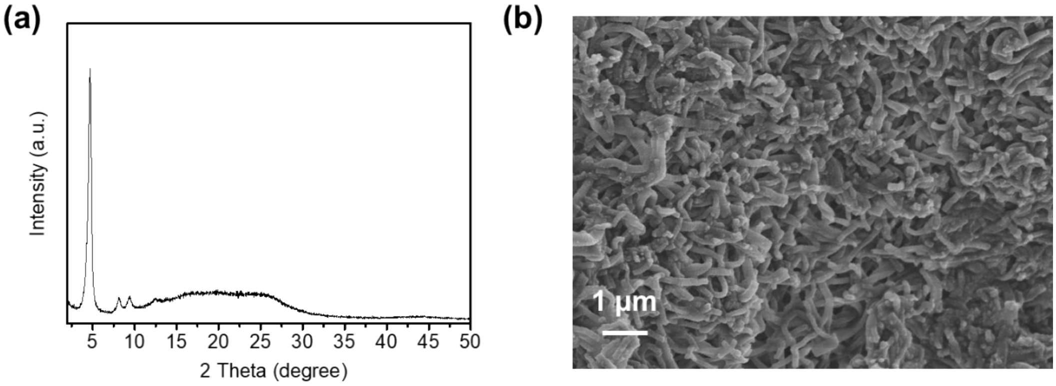

Figure S3. (a) XRD patterns and (b) SEM image of COF-LZU1-NT after calcination at 250°C for 1h under nitrogen atmosphere.

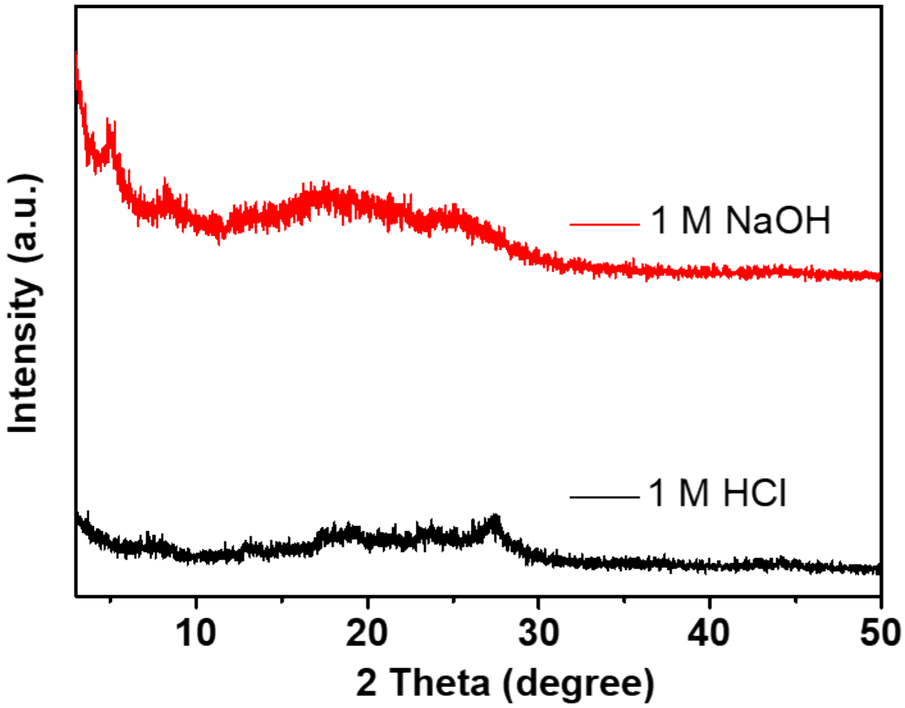

Figure S4. XRD patterns of COF-LZU1-NT after treatment in different conditions.

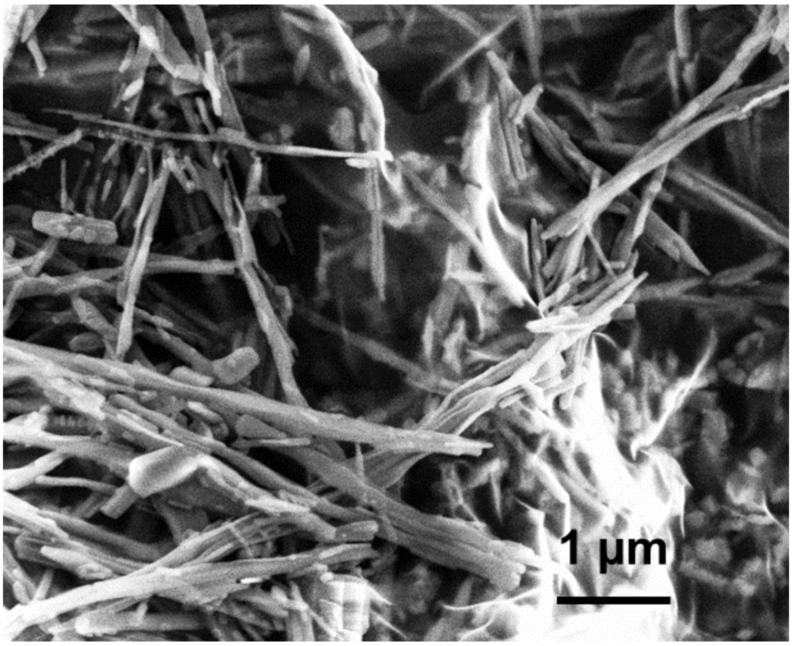

Figure S5. SEM image of TMA self-assemblies

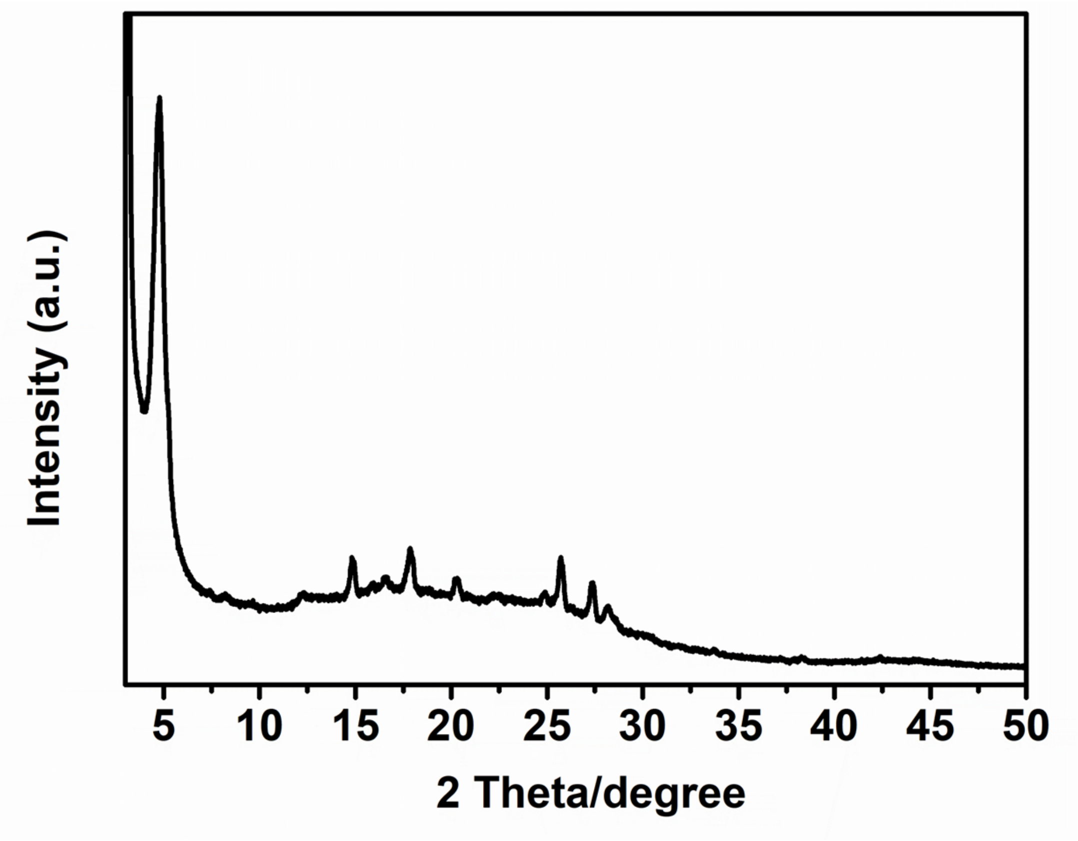

Figure S6. XRD pattern of COF-LZU1-NT with TMA template inside.

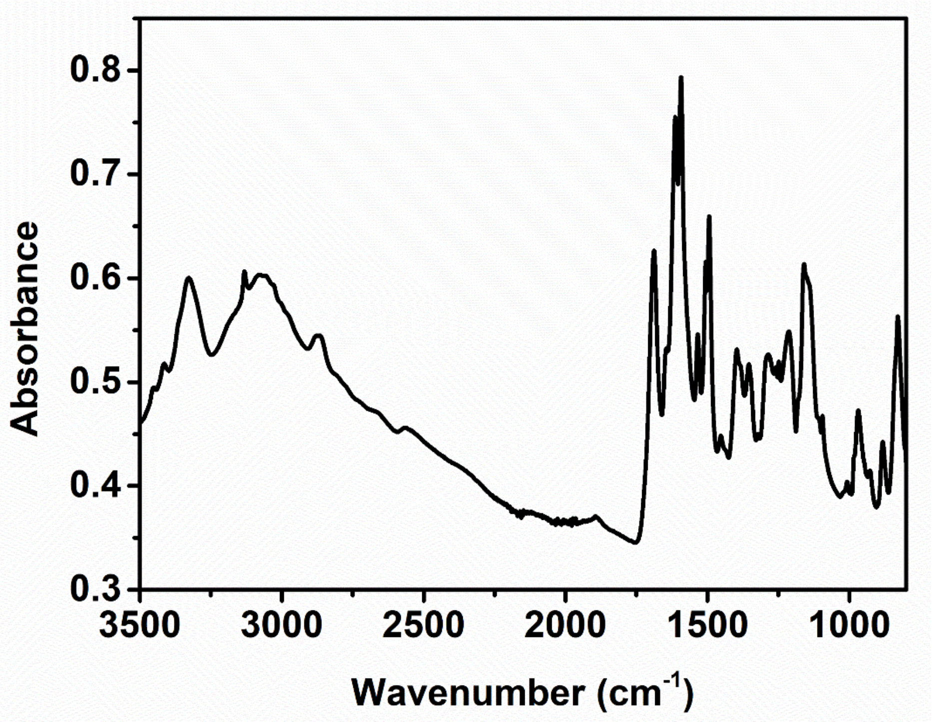

Figure S7. FTIR analysis of COF-LZU1-NT with TMA template inside.

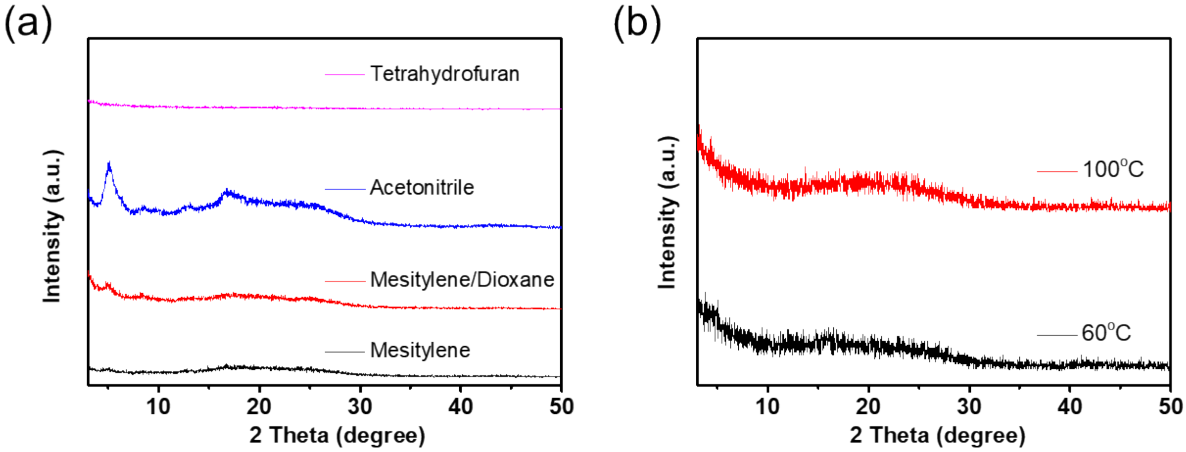

Figure S8. XRD patterns of COF-LZU1-NT synthesized under (a) various solvents and (b) different temperatures.

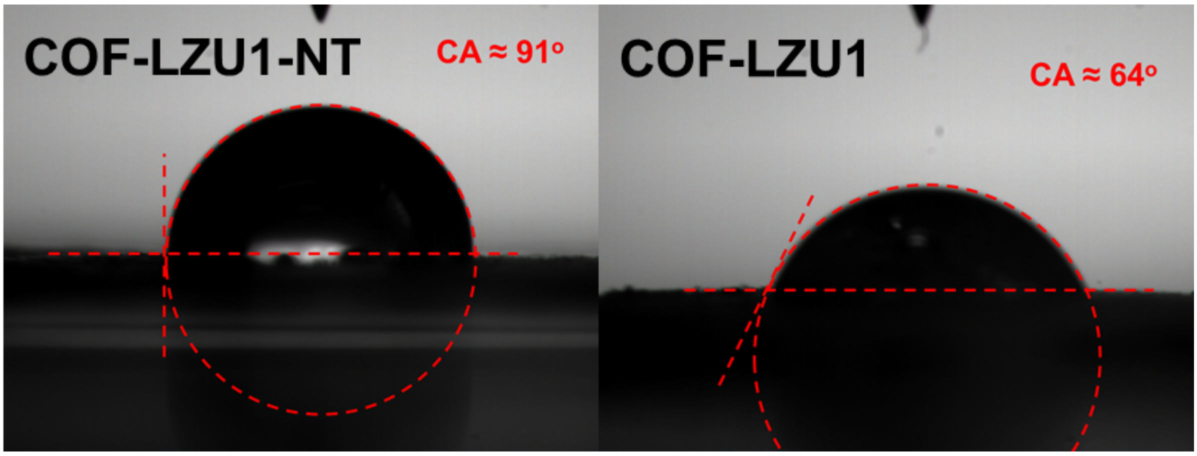

Figure S9. Contact angle of COF-LZU1-NT and COF-LZU1