

Supporting Information

Surface Growth of Highly Oriented Covalent Organic Framework Thin Film with Enhanced Photoresponse Speed

Ying Chen,^{ab} Haijun Cui,^{ab} Jianqi Zhang,^b Kun Zhao,^b Defang Ding,^b Jun Guo,^b Lianshan Li,^{*b}
Zhiyuan Tian,^{*a} and Zhiyong Tang^{*b}

Correspondence should be addressed to Lianshan Li (lils@nanoctr.cn), Zhiyuan Tian
(zytian@ucas.ac.cn), and Zhiyong Tang (zytang@nanoctr.cn)

Table of contents

Materials and Methods	S1
Synthesis Methods	S2
Supplementary Spectra Data	
FT-IR spectrum of TT-COF powder	S4
Nitrogen sorption isotherm of TT-COF powder	S5
Thermo gravimetric analysis of TT-COF powder	S6
Absorption spectrum of oriented TT-COF films	S7
I–V profile of in situ growth TT-COF film	S8
Photocurrent of in situ growth TT-COF film	S9
SEM images of oriented TT-COF films	S10
AFM images of oriented TT-COF films	S11

Materials and Methods

All materials were used without purified. Thieno[3,2-b]thiophene-2,5-diylidiboronic acid was purchased from Heowns company, polyol 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP), n-butyllithium, dimethyl formamide, isopropyl borate, 1,4-dioxane and 1,2,4-trimethylbenzene were purchased from J&K company, and N-bromosuccinimide was purchased from Alfa company.

¹H NMR (400 MHz) spectra were obtained using a Bruker DMX-400 NMR spectrometer with tetramethylsilane as an internal standard. Absorption spectra were

recorded using a Hitachi U-3010 spectrophotometer. SEM images and optical images were obtained with a Hitachi S-4800 microscope and Leica DM4000M microscope. STEM imaging was carried out at 200 kV using a FEI Tecnai G2 F20 U-TWIN instrument. The GIWAXS samples were prepared on glass substrates following the same preparation conditions as those for devices. The data were obtained with an area Pilatus 100k detector that had a resolution of 195×487 pixels (0.172 mm × 0.172 mm) at an in-house X-ray scattering facility (Xenocs WAXS/SAXS system). The X-ray wavelength was 1.54 Å, and the incidence angle was 0.2°. The I-V curves of the devices were determined by a Keithley 4200 instrument and the photocurrent was obtained under a 300 W xenon lamp (Beijing Perfectlight Company) as a light source. TGA measurements were taken using a PerkinElmer Diamond TG/DTA calorimeter at a heating rate of 5°C min⁻¹ from 25°C to 900°C under N₂ flow after drying at 150°C for 24h. The nitrogen sorption isotherms were recorded on Micromeritics ASAP-2420 instrument. Prior to the measurement of the adsorption isotherm the sample was treated as follows. The product was soaked in dichloromethane for 12 h, separated by filtration and heated for 12 h at 150 °C under oil pump vacuum. The calculation of the pore size distribution was done using the NLDFIT model. Fourier transform infrared (FTIR) spectra were collected on a Spectrum One in the spectral range of 400-4000 cm⁻¹ using the KBr disk method. AFM images were obtained with a High Resolution Scanning Probe Microscope SPM-8000 (SHIMADZU Company).

Synthesis Methods

Synthesis of 2,5-dibromothiopheno[3,2-*b*]thiophene:

Thieno[3,2-*b*]thiophene (0.50 g, 3.57 mmol) was dissolved in DMF (10 mL) at 0 °C. N-bromosuccinimide (1.91 g, 10.70 mmol) was added and the reaction mixture stirred overnight. Water (500 mL) was added and the mixture extracted three times with ether. The organic phase was washed 4 times with water, dried (MgSO₄) and concentrated *in vacuo*. Flash column chromatographic purification on silica gel (pentane) afforded 4 (0.90 g, 85%) as a white solid.

¹H-NMR (400 MHz, DMSO-*d*₆): δ 7.61 (2H).

Synthesis of thieno[3,2-*b*]thiophene-2,5-diylidiboronic acid (TTBA):

2,5-dibromothiophene 4 (0.50 g, 1.7 mmol) was dissolved in THF (13.4 mL) and cooled to -80 °C. Then *n*-BuLi (2.62 mL, 1.6 M in hexane, 4.25 mmol) was added and the reaction mixture stirred for 45 min at that temperature. Triisopropyl borate (0.95 g, 5.10 mmol) was added dropwise at -80 °C and the mixture was allowed to warm to room temperature overnight. The reaction was quenched with 2 M HCl and the phases were separated. The aqueous phase was adjusted to pH 7 with 2 M HCl and then extracted with ethyl acetate (3 x 25 mL). The combined organic phases were washed with brine, dried (MgSO₄) and concentrated in vacuo. The resulting solid was washed with pentane and dried to afford a green-gray powder (210 mg, 55%) sufficiently pure for further manipulation.

¹H-NMR (400 MHz, DMSO-*d*₆): δ 8.36(4H), 7.85(2H).

Synthesis of TT-COF:

A conventional stainless steel autoclave equipped with a 20 ml teflon liner was charged with TTBA (11.6 mg, 0.051 mmol) and HHTP (11.0 mg, 0.034 mmol). The reaction mixture was suspended in 1 ml of a 1:1 v : v solution of mesitylene : dioxane and heated for 72 h at 150 °C. The dark grey precipitate was isolated by filtration and washed with dry acetone (30 ml).

FT-IR (KBr, cm⁻¹) : 3436(m), 1632(m), 1485(s), 1443(m), 1358(s), 1279(s), 1243(m), 1164(m), 1055(w), 853(m), 651(w).

Synthesis of TT-COF film:

The method is similar to that of TT-COF powder. The teflon shelf with the glass or silicon wafer was immersed horizontally into the mixture of precursor solution in a 20 ml teflon liner. The precursor solution is consist of TTBA (11.6 mg, 0.051 mmol) and HHTP (11.0 mg, 0.034 mmol) suspended in 5 ml of a 1:1 v : v solution of mesitylene : dioxane and heated for 20 h at 150 °C. The brown substrate was isolated and washed with dry acetone (30 ml).

Supplementary spectra data

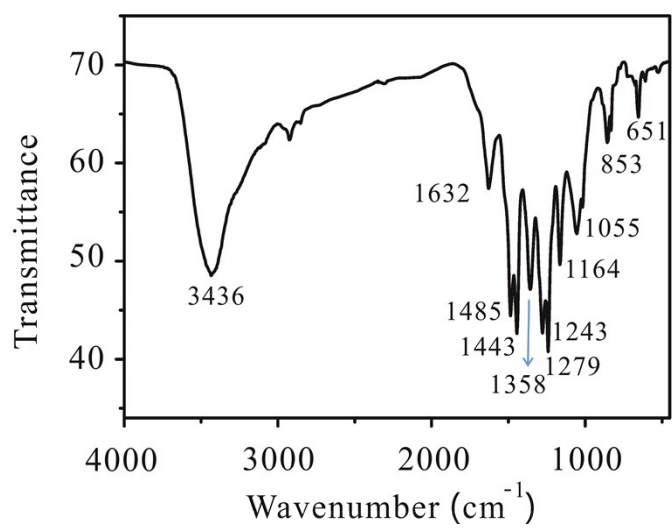


Figure S1. FT-IR spectrum of TT-COF powder

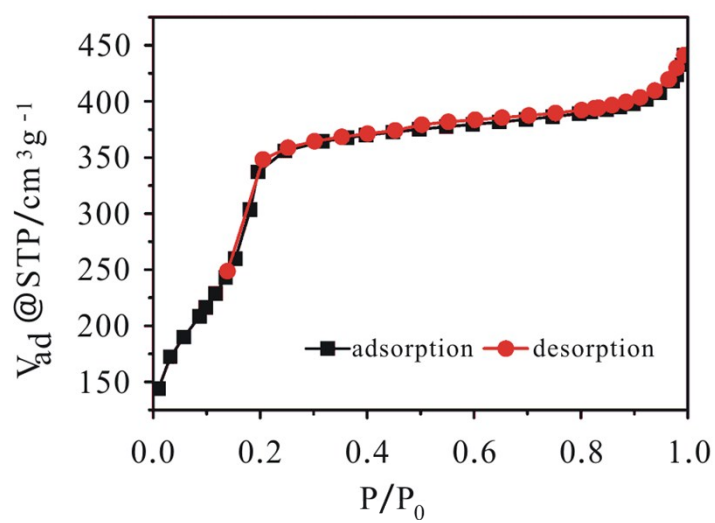


Figure S2. Nitrogen sorption isotherm of TT-COF powder

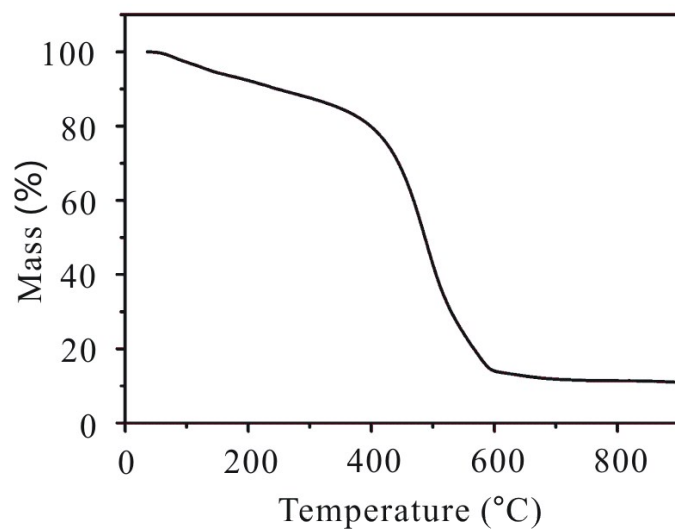


Figure S3. TGA of TT-COF powder

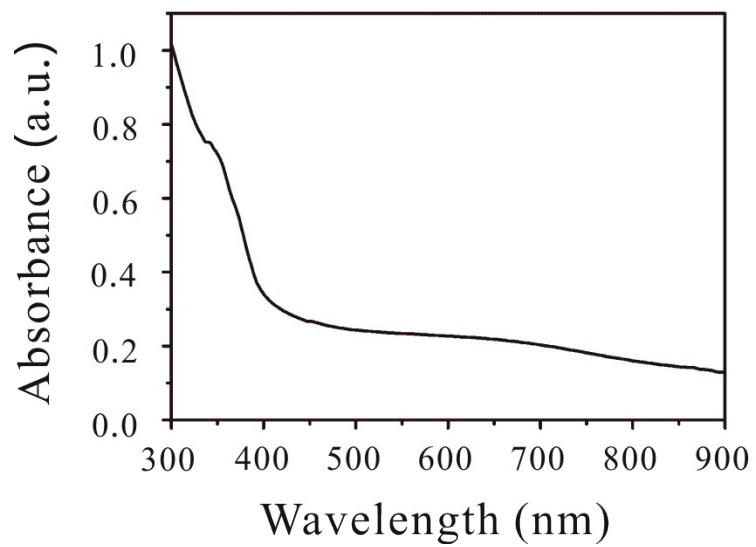


Figure S4. Absorption spectrum of oriented TT-COF films

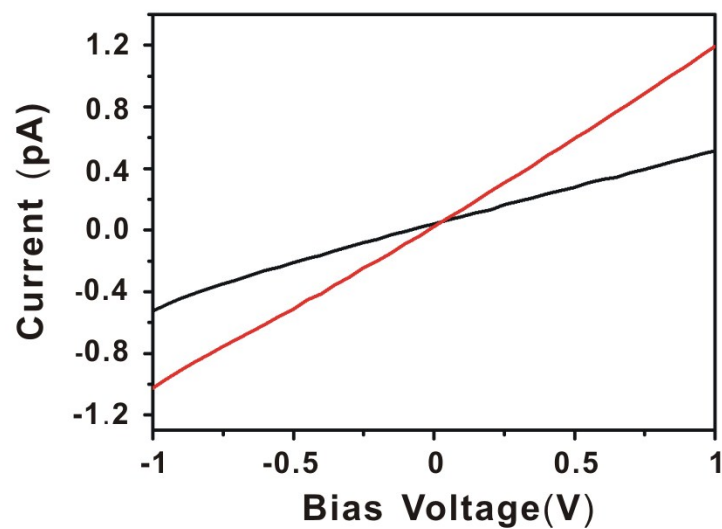


Figure S5. I-V profile of a 50 μm width Au gap of in situ growth TT-COF film device (black curve: without light irradiation; red curve: upon light irradiation).

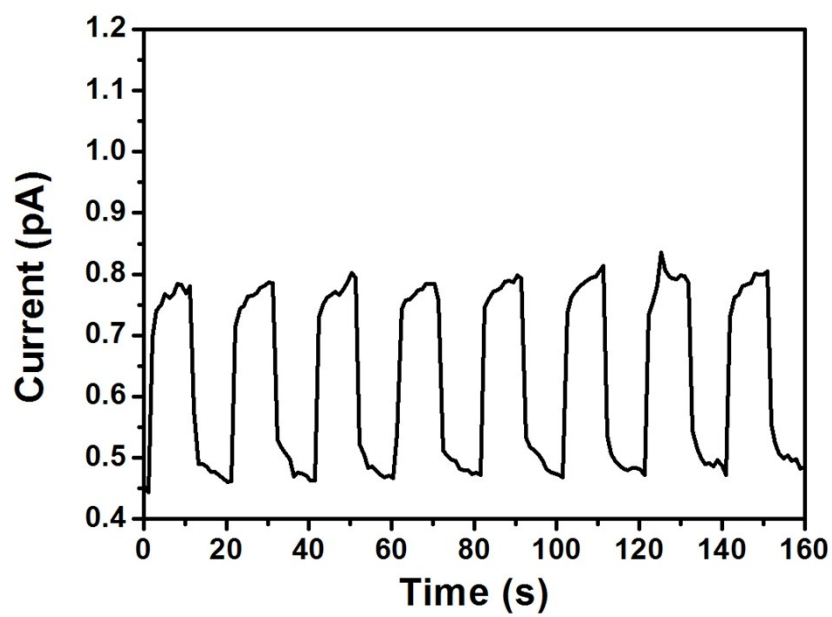


Figure S6. The photocurrents for in situ growth TT-COF film upon repeated switching of the light on and off after being stored in the glove box for 1 week.

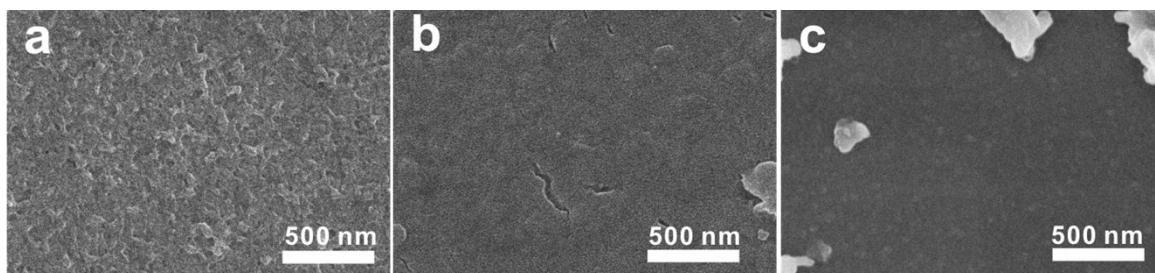


Figure S7. Top-view SEM images of TT-COF with different growth time: (a) 4h, (b) 6h, and (c) 17h.

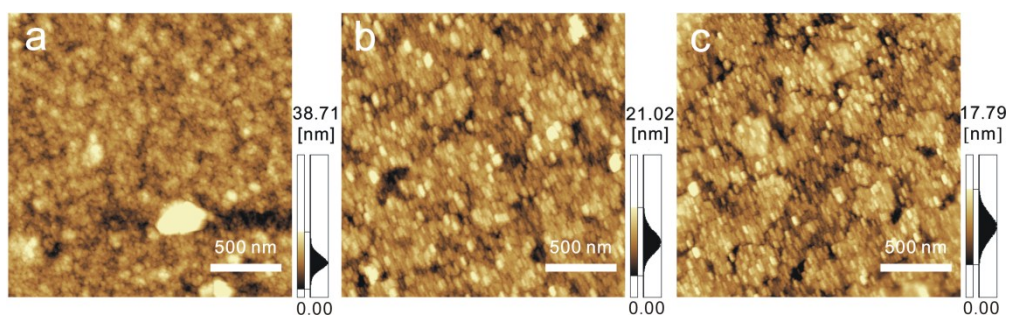


Figure S8. Tapping-mode AFM images of TT-COF with different growth time: (a) 4h, (b) 6h, and (c) 17h.