Supplemental information

Detachable all-carbon-linked 3D covalent organic framework films for semiconductor/COF heterojunctions by continuous flow synthesis

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**Figure S1.** The frequency shift of the Cu coated QCM chip in pure pyridine flow at different speeds.
Figure S2. The evidence for the formation of ionic Cu species in pyridine. (a) Pure pyridine. (b) Pyridine solution prepared by immersing a Cu substrate at 50 °C for 10 hours. (c) The same pyridine solution as in (b) after two drops of Na(OH)$_2$ (1M, aq) were added. The blue precipitation is Cu(OH)$_2$.

Figure S3. The frequency shift of the Cu coated QCM when flowing SBFyne dissolved in pyridine (0.5 ml/h) at different temperatures in the flow cell chamber.
Figure S4. (a) Real time monitoring of the film growth by QCM under flow of monomer solutions having different concentrations. The rate of film growth is proportional to the derivative of the curves. The experiments were conducted at 50 °C, with a flow rate of 0.8 mL/h. (b) Real time monitoring of the film growth by QCM for different total reaction times. The film thickness is proportional to the total frequency shift in the experiment. The film thicknesses ($f_1$-shift ≈ 1/2 $f_2$-shift ≈ 1/3 $f_3$-shift) are linearly proportional to the film growth times ($t_1 = 1/2 t_2 = 1/3 t_3$). The experiments were conducted at 50 °C, with a flow rate of 0.8 mL/h.
Figure S5. AFM height image of the Cu coated QCM chip used for preparing the SBFdiyne-COF film in the substrate catalyzed synthesis in continuous flow.

Figure S6. Comparison of FTIR absorptions at 3281 cm$^{-1}$ for SBFdiyne-COF and SBFyne monomer.
Figure S7. (a) XPS of a SBFdiyne-COF film prepared by substrate-catalyzed synthesis in continuous flow, and (b) zoom-in spectra in the range of 850 eV-1030 eV. The film sample was transferred onto a SiO$_2$/Si substrate prior the measurement. The quantitative analysis of XPS shows detected C atomic% of 26.5% and detected Cu atomic% of 0.3%, which gives a corrected Cu atomic% of 0.6%, neglecting the signals from the surface and taking the molecular formula of the SBFdiyne-COF into account (C$_{37}$H$_{20}$O$_4$).

Figure S8. (a) Selected area electron diffraction (SAED) of an SBFdiyne-COF film. The table gives d-spacing of diffraction rings. (b) GIXRD of the SBFdiyne-COF film prepared in the substrate catalyzed synthesis in continuous flow. The table gives d-spacing of diffraction peaks. The d$_3$ SAED diffraction corresponds to a 2θ value of 16.9° in the GIXRD spectrum. This peak is not spectrally resolved but is hinted as a shoulder on the P3 peak.
Figure S9. (a) Structure of the SBFdiyne-COF with dia topology in absence of interpenetration (from reference 25), together with the distance between the main lattice plane, which is about four times of the measured d-spacing of 2.5 Å, suggesting a possible four-fold interpenetration. (b) Illustration of four-fold interpenetration of dia topology. A 3D COF contains voids that run through in all three dimensions. This enables frameworks, not covalently connected, that grow in each other voids. The discrepancy of a factor four between the d-spacing of the experimental data and the model shown in (a) thus indicates a four-fold interpenetrated structure. Interpenetration is here schematically illustrated as four frameworks with their unit cells translated a quarter of a unit cell between each other.
Figure S10. The I-V curve of a SBFdiyne-COF film.

Figure S11. (a) AFM height image of a DPP4T film on top of a SBFdiyne-COF film (the surface of the DPP4T/SBFdiyne-COF heterojunction). (b) AFM height image of a single layer DPP4T film.
Figure S12. A p-n junction and their energy band diagram under (a) zero bias (equilibrium state), (b) reversed bias, and (c) forward bias. The energy levels of the SBFdiyne-COF were determined from the optical band gap (Figure S13) and UPS width (Figure S14).

Figure S13. Tauc plot of a SBFdiyne-COF film for the optical band gap determination. $\alpha$ is the absorption coefficient and $hv$ is the photon energy.
Figure S14. The UPS spectrum of a SBFdiyne-COF film. The edges of the UPS spectrum are given by intersection of two dashed blue lines of the tangents and the baseline, from which the UPS width is determined.
Supplemental Experimental Procedures

Chemicals

All starting materials and solvents were purchases from Sigma-Aldrich or VWR and used without any purification. Pyridine used for continuous flow synthesis was purchased as Aldrich Sure/Seal™ packages. 3,3’,6,6’-tetraethynyl-2,2’,7,7’-tetramethoxy-9,9’-spirobifluorene (SBFyne, the monomer) was synthesized according to the literature reported procedure and stored in a glovebox at -20 °C.[S2]

Fabrication of SBDdiyne-COF Film (Substrate-catalyzed synthesis in Continuous Flow)

For SBFdiyne-COF films fabrication on QCM Cu sensor, a Q-Sense E1 Quartz Crystal Microbalance (QE 401 Electronic unit/ Module QFM 401/QCP 101 Chamber platform) from Biolin Scientific (with Kalrez® O-rings and gaskets) was used. QCM Cu sensors were purchased from Biolin Scientific (surface roughness < 4 nm, protected in inert atmosphere). The QCM sensor with Cu surface was sealed in the mixing chamber of the sensing module. The SBFyne monomer solution (0.1 mg/mL, in pyridine) was prepared in a glovebox and transferred out before the reaction. Then the SBFyne solution and pure pyridine were loaded in two separate injection channels (Fig. 1a). The continuous flow system was initially rushed with the solvent pyridine to exclude air. At a constant pyridine flow rate of 0.5 mL/h, the temperature of the mixing chamber was increased to 50 °C and kept there for 5 min until the QCM signal stabilized. Then, the SBFyne solution was injected with a flow speed of 4.0mL/h for 2 min to quickly fill the system, followed by a constant injection speed of 0.5mL/h for stable film growth. When the frequency shift reached 2700 Hz, the injection of SBFyne was terminated and pyridine was injected at 4.0mL/h to wash away unreacted reactants. At this stage the chamber was cooled down to 20 °C, and air was flushed through the system in order for it to dry. Finally, the QCM sensor with the fabricated film was dried by a nitrogen flow for further characterization. To detach the film from the QCM sensor, the as-prepared film was taken from the reaction chamber and flushed with ethanol from a squeeze bottle, and the exfoliated film in the liquid was collected in a beaker. The film in the liquid can be transfer to the wanted substrate (for instance a wafer) by using the corresponding substrate to fish the film up.

Film characterization

The macroscopic observation of films were conducted using a Zeiss Axioscope 5 in reflective mode. The film morphology and surface roughness measurements were conducted on a NT-MDT NTEGRA AFM in tapping mode using a silicon cantilever (Tap150Al-G from Budget Sensors). SEM were carried out using a JEOl JSM-6301F scanning electron microscope with an acceleration voltage of 12 kV. TEM were carried out using FEI Tecnai T20 transmission electron microscope with a LaB6 electron source under the acceleration voltage of 200 kV. Grazing incidence WAXS data were obtained on a Mat:Nordic SAXSLAB instrument. The detector used was a Pilatus3 300K R from Dectris, and the source was a Rigaku Micromax -003 with a Cu target. All measurements were carried out at a pressure of approximately 0.1 mbar in the entire flightpath. The sample to detector distance was set to 127 mm, and the incidence angle was varied between 0.2 and 0.4°, depending on the sample. Exposure times varied from 1 to 4 hours, depending on the sample. Before each measurement, a calibration of the sample tilt was performed with a z-scan and a rocking curve. The XPS analysis was performed on an ESCALab 250Xi (Thermo Scientific) using 200 W monochromatized Al Kα radiation. The UPS analysis was performed on instrument Nexsa from ThermoFisher Scientific. Raman spectra were measured using a WITec alpha300 R Raman Microscope equipped with a 532 nm laser. FTIR spectra were measured on a Bruker Invenio R instrument in transmission mode.

Heterojunction construction and electrical characterization

The SBFdiyne-COF film was transferred to a silicon wafer with predeposited Au electrode pattern, the DPP4T layer was fabricated on top of the COF-film by spincoating 10 µL DPP4T solution(5.0mg/mL) at a speed of 500 rpm (30s) followed by a speed of 2000 rpm (3 min). Then the top Au electrodes were prepared by Au sputtering through the mask. The diode with single DPP4T layer in the middle was prepared by the same method for comparison. I-V curves were measured using a Keithley 2600B SMU at ambient conditions.
Supplemental References

[S1] Zhang, T., Hou, Y., Dzhagan, V., Liao, Z., Chai, G., Löfler, M., Olianas, D., Milani, A., Xu, S., Tommasini, M., et al. (2018). Copper-surface mediated synthesis of acetylenic carbon-rich nanofibers for active metal-free photocathodes. Nat. Commun. 9, 1140.

[S2] Pop, L., Dumitru, F., Hădade, N. D., Legrand, Y.-M., van der Lee, A., Barboiu, M., Grosu, I. (2015). Exclusive Hydrophobic Self-Assembly of Adaptive Solid-State Networks of Octasubstituted 9,9′-Spirobiﬂuorenes. Org. Lett., 17, 3494-3497.