Supporting Information

2D oriented covalent organic frameworks for alcohol-sensory synapse

Teng Li, Hongliang Yu, Ziyu Xiong, Zhan Gao, Ye Zhou and Su-Ting Han*

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Experimental Methods

COF RRAM device fabrication. At first, COF-5 film was synthesis by HHTP (0.049 mmol, 16 mg) and PBBA (0.15 mmol, 25 mg) in a 15 mL cylindrical pressure vessel with 1 ml mixture solvent of mesitylene/dioxane (1:1 v/v). After sealing, the mixed reactants were sonicated for 30 min at low temperature. The vessel was opened in the glove box and a 3 mm thick ring-shaped Teflon holder was added, the ITO glass was placed on the holder with the ITO side facing down. The vessel was then heated for 9 h at 90 °C. The substrates were then separated, the powder was filtrated and dried under vacuum. The ITO glass was soaked in anhydrous toluene overnight, and dried under vacuum. The synthesis process of COF-1 film was similar to that of COF-5, the substrate was PBBA (0.3 mmol, 50 mg) and the temperature rose to 100 °C. COF-10 was synthesized by HHTP (0.049 mmol, 16 mg) and BPDA (0.15 mmol, 36 mg), the other reaction conditions were the same as synthesis of COF-5.

Finally, the fabricated COF film was dried under vacuum under 60 °C. And then patterned Ag electrode was thermal evaporated with a mask on the COF film.

Characterization of devices. The as-prepared COF powder were characterized by XRD on Bruker D8 Advance X-ray diffractometer using Cu-K α radiation ($\lambda = 1.5418$ Å). AFM image of COF-5 film was achieved by Bruker Dimension Icon under clean and dry ambient condition. GIWAXS experiment was carried out on Xenocs Xuess 2.0 beamline. The incident X-ray angle is 0.2 degrees and the wavelength is 1.54 angstrom. The scattered signal was tested by Pilatus 1M detector with 150 mm distance from sample to detector. The diffraction data were analyzed by using the Nika software package for Wavemetrics Igor and WAXS tools. The wavelength of incident beam is $\lambda = 0.154$ nm (Cu K α) with the sample–detector distance of 168.15

mm. The top-view and cross-sectional SEM images were completed by the fieldemission SEM (MERLIN compact, Carl Zeiss). The TEM images were taken with the HRTEM (FEI Titan Cubed Themis G2 300). The electrical properties of devices were measured by Keithley 4200-SCS at room temperature.



Fig. S1 The XRD pattern for COF-5 powder (a) and film grown on ITO (b).



Fig. S2 The GIWAX images for COF-5 powder (a) and film (b).



Fig. S3 The function diagram of cell area of Ag electrode and resistance in HRS and LRS.



Fig. S4 The retention time of COF-5 RRAM device.



Fig. S5 The thickness of COF-5 film with different reaction time.



Fig. S6 The performance of COF-5 devices based on 50 nm thick silver electrode affected by different COF-5 film thickness.



Fig. S7 The performance of COF-5 devices based on 120 nm thick COF-5 film affected by different Ag electrode thickness.



Fig. S8 a) Map of RESET voltages displayed by optical micrographs of 100 COF-5 devices divided into two parts. b) Histogram of spatial RESET voltage distribution.



Fig. S9 a) HAADF STEM image of vertical COF-5 device. b) EDS element analysis of the red dotted line areas in a. c) The EDS mapping images of the Ag filament region in a with different elements.



Fig. S10 The real-time current diagram of the device in different alcohol atmosphere with 600ppm (a), 800ppm (b) and 1000 ppm (c) concentration.



Fig. S11 Illustrations of adsorption and desorption of guest molecules in COF RRAM device. At first, the device is reset to HRS with space between the filament and top electrode. With the adsorption of guest molecules, the filaments at the bottom and enough guest molecules connect the top and bottom electrodes to make the device reach intermediate state. After set process, the Ag atoms at the bottom transform to the top electrode, thus extruding the adsorbed guest molecules out of the channel.