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Interface-confined Synthesis of a Nonplanar redox-active Covalent Organic Framework Film for Synaptic Memristors

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Materials

Tris(4-formylphenyl)amine (TFPA) was synthesized following the previously reported literature protocols.¹ Sc(OTf)₃ (98%), p-toluenesulfonic acid (PTSA, \geq 99%), acetic acid (AcOH, \geq 99.5%), tris(4-aminophenyl)-amine (TAPA, 97%) were purchased from Macklin. Dichloromethane (DCM), ethanol (EtOH) with analytical purity was purchased from Aladdin. All reagents and solvents were used as received without further purification.

Instruments

Fourier transform infrared (FTIR) spectra were recorded by Spectrum 100 spectrophotometer (Perkin Elmer, Inc., USA). Ultraviolet/visible (UV/Vis) absorption spectra were measured on a Shimadzu UV-2540 spectrophotometer. Powder X-ray diffraction patterns (PXRD) were recorded on a Bruker D8 Advance diffractometer with Cu-K α 1 radiation (λ =1.5406 Å). The scanning electron microscopy (SEM) images were recorded on a field emission scanning electron microscope (FESEM, Carl Zeiss Gemini) operating at an accelerating voltage of 3 kV. High magnification transmission electron microscopy (TEM) was performed using a JEOL-2100 (JEOL Ltd., Japan) TEM system operating at an accelerating voltage of 200 kV. ¹³C crosspolarization/magic angle spinning solid-state nuclear magnetic resonance (CP/MAS ssNMR) experiments were performed on a Bruker AVANCE III 400 WB spectrometer operating at 100.62 MHz for 13C using a double resonance 4 mm MAS NMR probe and a sample spinning rate of 10 kHz. The cross polarization time was 1 ms. The chemical shifts were referenced with adamantane. Thermal gravimetric analyses (TGA) were performed on a Perkin-Elmer TGA-7 thermogravimetric analyzer in nitrogen atmosphere from ambient temperature to 800 °C at the rate of 10 °C min⁻¹. UV–vis diffuse reflectance spectra (UV–vis DRS) were

recorded at room temperature on a HITACHI U-4100 Spectrophotometer. Nitrogen physisorption analyses were performed at 77 K using Quantachrome autosorb iQ3 equipment. ¹H NMR spectra were recorded on a Bruker AVANCE 400 NMR spectrometer, operating at frequencies of 400 MHz using CDCl₃ as solvent. X-ray photoelectron spectroscopy (XPS) experiments were carried out on an AXIS Ultra DLD system from Kratos with mono Al Kα radiation (1486.6 eV) as X-ray source, the C 1s value was set at 284.6 eV for charge corrections. EPR experiments were performed using a Bruker EMX-Nano Benchtop spectrometer equipped with a continuous-flow nitrogen cryostat.

Experimental Section

Fabrication of TFPA-TAPA COF films

The optimal synthesis procedure was as follows: TAPA (174.3 mg, 0.6 mmol) and TFPA (197.4 mg, 0.6 mmol) were separately dissolved in 100 ml of DCM as the organic phase. The TAPA and TFPA solutions were poured into a beaker together as the organic phase, and then pure water was slowly added onto the top surface of the DCM solution, leaving a stable DCM/water interface. Subsequently, *p*-toluenesulfonic acid (310 mg, 1.8 mmol) was gently added into the aqueous phase as the acid catalyst. Afterward, the beaker was covered to keep it stable and avoid airflow. A transparent and smooth thin film was clearly observed at the interface between the two immiscible phases. After an interfacial reaction at room temperature for 72 h, the water was pumped out slowly, and the thin film was floated on the DCM solution with approximately 17% yield. The thin film was transferred to an ITO substrate, which was carefully pre-cleaned sequentially with deionized water, acetone, and 2-propanol in an ultrasonic bath for 15 min. Then it was rinsed several times with ethanol and DCM to wash away residual monomers. To completely remove monomers, the film supported by ITO was immersed in DCM for 10 h. The clean film was used to further characterize and fabricate devices.

Fabrication of the TFPA-TAPA films using the other catalysts

TAPA (174.3 mg, 0.6 mmol) and TFPA (197.4 mg, 0.6 mmol) were separately dissolved in 100 ml of DCM as the organic phase. The TAPA and TFPA solutions were poured into a beaker together as the organic phase, and then pure water was slowly added onto the top surface of the DCM solution, leaving a stable DCM/water interface. Subsequently, $Sc(OTf)_3$ (0.6 mmol) or acetic acid (1.8 mmol) were gently added into the aqueous phase as acid catalysts. Afterward, the beaker was covered to keep it stable and avoid airflow. A transparent and smooth thin film

was clearly observed at the interface between the two immiscible phases. After an interfacial reaction at room temperature for 72 h, the thin film was processed like the above steps.



Figure S1. Fourier-transform infrared (FTIR) spectroscopy.



Figure S2. (a) XPS spectra of TFPA-TAPA. (b) The high-resolution XPS C 1s spectra. (c) The high-resolution XPS N 1s spectra.



Figure S3. The SEM images of TFPA-TAPA after different reaction times: (a) 3 h; (b) 6 h; (c) 12 h; (d) 72 h.



Figure S4. X-ray diffraction patterns of TFPA-TAPA films prepared by different catalysts.



Figure S5. The (100) plane in powder X-ray diffraction patterns of the TFPA-TAPA film immersed in various solvents for 12 h.



Figure S6. The (100) plane in the powder X-ray diffraction (PXRD) patterns after acid (1 M HCl) and base (1 M NaOH) treatment for 12 h. The results indicated that the crystallinity was seriously deteriorated by 1 M HCl.



Figure S7. The UV-Vis absorption spectra of TFPA, TAPA, and TFPA-TAPA film.



Figure S8. UV-Vis DRS spectrum of the TFPA-TAPA film. Inset: the plot of the Kubelka-Munk function used to extract the band gap.



Figure S9. UPS spectra of TFPA-TAPA films.



Figure S10. Energy band positions of TFPA-TAPA films.



Figure S11. The eclipsed (AA) stacking mode of TFPA-TAPA.



Figure S12. The current-voltage characteristics of the (a) Al/TAPA/ITO and (b) Al/TFPA/ITO devices.

When the electronic device was applied nine consecutive negative sweep voltages from 0 to -1 V and then back to 0 V, the observed device current was found to decrease incrementally from -3.16 to -3.74 mA (read at -1 V). After that, the device was applied nine consecutive positive voltage sweeps of 0 V to -1 V to 0 V, and the device current decreases gradually from 2.46 to 1.76 mA (read at 1 V). At the same conditions, the device current of Al/TFPA/ITO can decrease with a very small current change as shown in **Figure S12b**.



Figure S13. Current-voltage characteristics of the Al/amorphous TFPA-TAPA/ITO device in a sweeping range of ± 1 V.



Figure S14. (a, b, c) The cross-sectional SEM images of TFPA-TAPA film with different active layer thicknesses. (d, e, f) The effect of film thickness on the current-voltage characteristics. (a and d) 40 nm. (b and e) 87 nm. (c and f) 205 nm.



Figure S15. Current-voltage characteristics of two random Al/TFPA-TAPA/ITO devices in a sweeping range of ± 1 V.

Sample	$S_{BET} (m^2/g)^{a}$	V _{Tot} (cm ³ g ⁻¹) ^{b)}	V _{micro} (cm ³ (STP) g ⁻¹) ^{c)}	D _{av} (nm) ^d
TFPA-TAPA	147.02	0.3032	33.779	8.2493

Table S1. N₂ physisorption results of TFPA-TAPA.

a) Specific surface area measured by BET model; b) The total pore volume measured at $P/P_0 = 0.99$; c) The microporous volume analyzed by t-plot method; d) Average pore size

Table S2. Fractional atomic coordinates for the eclipsed AA-stacking unit cell of TFPA-TAPA film.

Space group	P3			
Calculated unite cell	$a = b = 21.1721$ Å, $c = 4.3005$ and $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$			
Atom	X	У	Z	
C1	0.74601	0.37711	0.02972	
C2	0.8581	0.48646	-0.12855	
C3	0.90002	0.46119	0.01868	
H4	0.8845	0.53822	-0.24981	
C5	0.25436	0.61944	-0.02159	
C6	0.14554	0.50618	-0.17373	
C7	0.10099	0.52764	-0.02051	
H8	0.12172	0.45439	-0.29456	
C9	0.33073	0.77884	-0.17743	
C10	0.43092	0.79101	0.13539	
C11	0.46176	0.86675	0.13354	
H12	0.45913	0.76806	0.25748	
C13	0.66239	0.21793	-0.12744	
C14	0.56435	0.21109	0.18487	
C15	0.52942	0.13501	0.17757	
H16	0.53858	0.23628	0.30911	
C17	0.45763	0.97865	0.9796	
N18	0.52731	1.02208	1.01226	

H19	0.28015	0.74632	-0.29938
H20	0.51246	0.89996	0.25683
H21	0.7136	0.24843	-0.24737
H22	0.47833	0.10358	0.30036
H23	0.42192	1.00065	0.93565
N24	0.33333	0.66667	0.97798

Reference

1 Y.-X. Wang and M.-k. Leung, *Macromolecules*, 2011, 44, 8771-8779.