Supporting Information for

Single-displacement Controlled Spontaneous Electrolysis towards CuTCNQ Microribbon Electrodes in Organic Single-crystal Transistors

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Experimental Section

CuTCNQ crystal growth: The solution of TCNQ:$CuCl_2$ (anhydrous) with the molar ratio of 1:2 in acetonitrile was under ultrasonication for 30 min to offer a reactive medium, subsequently zinc plates were saturated into this solution for one hour to complete the following reactions: $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$, $Cu + TCNQ \rightarrow CuTCNQ$ (Fig 2a) By using single-displacement controlled spontaneous electrolysis, the 1D CuTCNQ in phase I was obtained.

9, 10–bis(2-phenylethynyl)anthracene (BEPA) crystal growth: We used heavily doped n-type silicon wafers with 300-nm-thick thermally grown oxide layer as the substrates, which were stepwise rinsed by hexane, chloroform and *iso*-propanol. Single crystals of BEPA were grown directly on the bare SiO_2/Si substrates by the drop-casting of the chlorobenzene solution (1mg/mL). After one or two days, the solvent was then removed by annealing process (80℃, 40min) to afford the thesingle-crystals for devices fabrication.

Device fabrication: This process was done in the Micromanipulator 6150 probe station with a high-resolution microscope (magnification scope of 400-1000 times). For copper or gold source/drain electrodes, we first adopted the "organic ribbon mask" method[1] to reserve the conducting channel and then deposited the metal to form the source/drain electrodes. To fabricate the CuTCNQ 1D microribbon electrodes, the probe was applied to lay the microribbons onto the organic single crystals. Finally, the gold films were attached to the CuTCNQ 1D mircoribbons for the probe measurement.[2] The fabrication was carried out using the mechanical transfer method: we laid the CuTCNQ 1D microribbons between the BEPA single-crystals and the already attached gold film on the substrates.

Characterization: The infrared spectrum was measured by the FT-IR，PE2000. The

XPS characterization was conducted on KRATOS Axis Ultra DLD spectrometer which integrated with a monochromatized Al Kα X-ray source (1486.6 eV) and a hemispherical analyzer (base pressure < 2×10^{-9} Torr). X-ray diffraction (XRD) measurements were carried out in the reflection mode using a Rigakuraix Rapid IP area detector X-ray diffraction system (Mo Kα radiation, λ = 0.71073 Å). SEM images were captured on a Hitachi S-4800 FESEM. Our device measurements were assisted by the Keithley 4200-SCS test system measured in ambient conditions. Furthermore, for the measurement of the mobility of devices, we calculate in the following manner: when the devices work in the saturated region, we have

$$\sqrt{I_{SD}} = \sqrt{\frac{WC_i}{2L}}\mu(V_G - V_T)$$

We regress with the derivation of $I_{SD}^{1/2}$ on V_G. Later taking account of the calculated slope, we obtain the mobility according to the following equation:

$$\mu = \frac{2L}{WC_i}\left(\frac{\partial\sqrt{I_{SD}}}{\partial V_G}\right)^2$$

Contact resistance characteristics: we have fabricated several arrays of devices: devices based on CuTCNQ source/drain electrodes in 4 arrays (including 12 devices each array), Au source/drain electrodes in 3 arrays (including 4 devices each array) and Cu source/drain electrodes in 4 arrays (including 12 devices each array). The statistics are shown in Table S1.

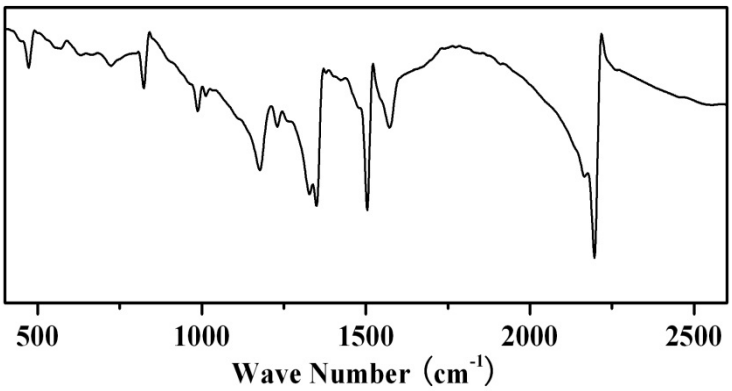

Figure S1 Infrared spectrum of CuTCNQ 1D microribbons

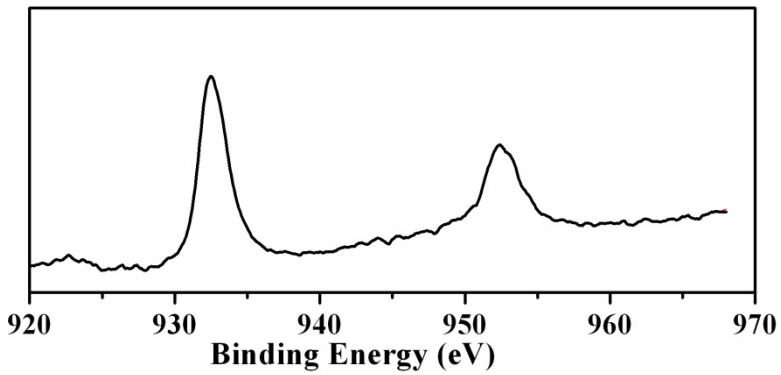

Figure S2 CuTCNQ 1D microribbons on XPS characterization

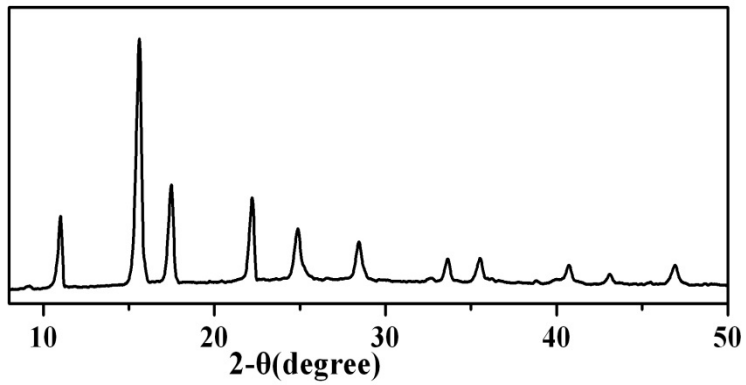

Figure S3 X-ray diffraction characteristics of CuTCNQ 1D microribbons

Table S1 The mobility and contact resistance statistics of BPEA single crystal devices based on different source/drain electrodes (CuTCNQ, Au and Cu) from four substrates.

	μ_{avg} [cm^2 /(V s)]	Rc·W (MΩ·cm)	$Rc \cdot W_{avg}$ (MΩ·cm)
CuTCNQ	0.16±0.013	0.82	0.86±0.03
	0.12±0.046	0.91	
	0.13±0.018	0.86	
	0.15±0.012	0.84	
Au	0.19±0.008	0.79	0.80±0.008
	0.19±0.003	0.81	
	0.20±0.005	0.80	
Cu	0.07±0.002	7.54	7.76±0.19
	0.068±0.001	8.05	
	0.067±0.002	7.81	
	0.069±0.001	7.63	

Table S2 The data of width-normalized total device resistance derived from output curve in linear region for CuTCNQ (12 devices), Au (4 devices) and Cu (12 devices) electrodes (W=2.4 μm) which is charted in Fig 5.d

CuTCNQ			Au			Cu		
L (μm)	R_{ON}·W (MΩ·cm)	μ [cm^2 /(V s)]	L (μm)	R_{ON}·W (MΩ·cm)	μ [cm^2/(V s)]	L (μm)	R_{ON}·W (MΩ·cm)	μ [cm^2 /(V s)]
1	6.79E4	0.11	2.2	3.19E5,	0.18	1.3	1.73E6	0.067
3	1.31E5	0.13	3.2	4.52E5,	0.19	2.2	2.39E6	0.067
5	1.69E5	0.15	3.8	5.07E5,	0.19	2.3	2.43E6	0.068
8	2.13E5	0.16	4.1	5.31E5,	0.20	2.5	2.53E6	0.068
10	2.50E5	0.18	/	/	/	3.2	3.34E6	0.068
12	3.03E5	0.17	/	/	/	3.2	3.36E6	0.070
15	3.73E5	0.16	/	/	/	3.7	3.67E6	0.070
18	3.80E5	0.16	/	/	/	3.8	3.80E6	0.070
20	4.13E5	0.15	/	/	/	4.1	3.98E6	0.071
21	4.32E5	0.17	/	/	/	4.3	4.15E6	0.070
25	5.06E5	0.16	/	/	/	4.9	4.32E6	0.072
28	5.22E5	0.14	/	/	/	5.1	4.41E6	0.073

References:

1 L. Jiang, J. H. Gao, E. J. Wang, H. X. Li, Z. H. Wang, W. P. Hu and L. Jiang, *Adv. Mater.* 2008, **20**, 2735.

2 Q. X. Tang, Y. H. Tong, H. X. Li, Z. Y. Ji, L. Q. Li, W. P. Hu, Y. Q. Liu and D. B. Zhu, *Adv. Mater.* 2008, **20**, 1511.