

## Supporting Information

# Solution-Processed    Self-Assembling    Charge-Transfer Cocrystal/TIPS-Pentacene    Heterojunctions    for    Artificial Synapses

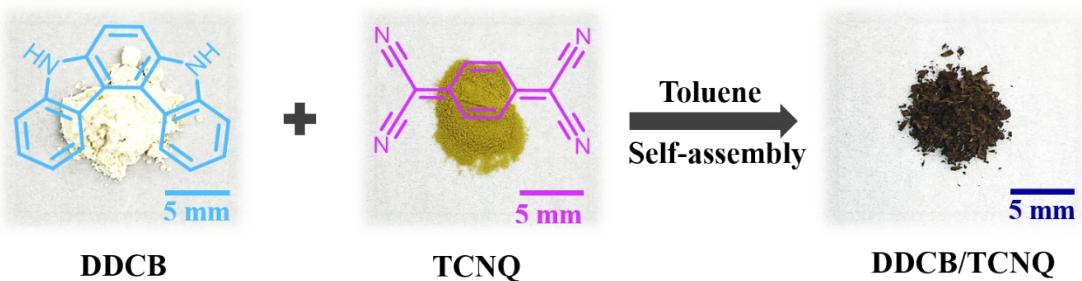
Tao Jin,<sup>a</sup> Wenju Li,<sup>a</sup> Yongyi Zhang,<sup>a</sup> Ruiheng Wang,<sup>a</sup> Shuai Wang,<sup>a</sup> Chen Pan,<sup>a</sup> Guan Wang,<sup>a</sup> Jiacheng Zhang,<sup>a</sup> Lei Yao,<sup>a</sup> Jing Zhang<sup>\*a</sup> and Qichun Zhang<sup>\*b</sup>

**\*Jing Zhang** - State Key Laboratory of Flexible Electronics (LoFE) & Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing 210023, China.

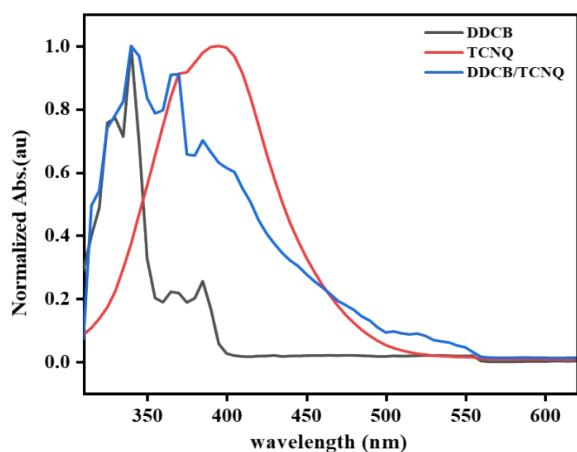
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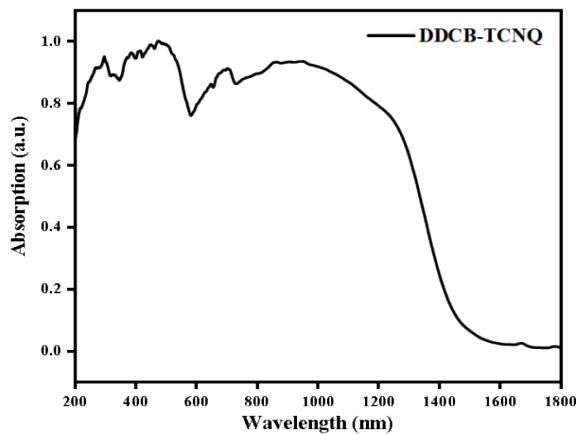
*E-mail:* qiczhang@cityu.edu.hk



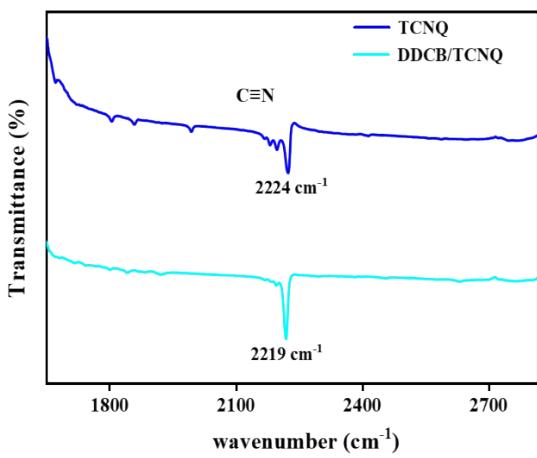
**Figure S1.** Schematic of the synthesis of DDCB/TCNQ cocrystals.



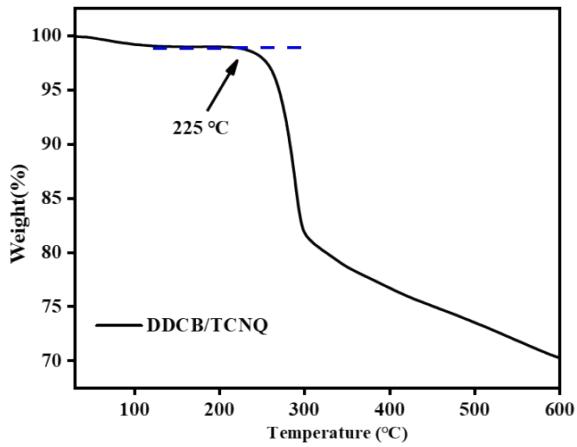
**Figure S2.** UV-Vis spectra of dilute solutions of DDCB, TCNQ, and a 1:1 DDCB/TCNQ mixture in toluene.



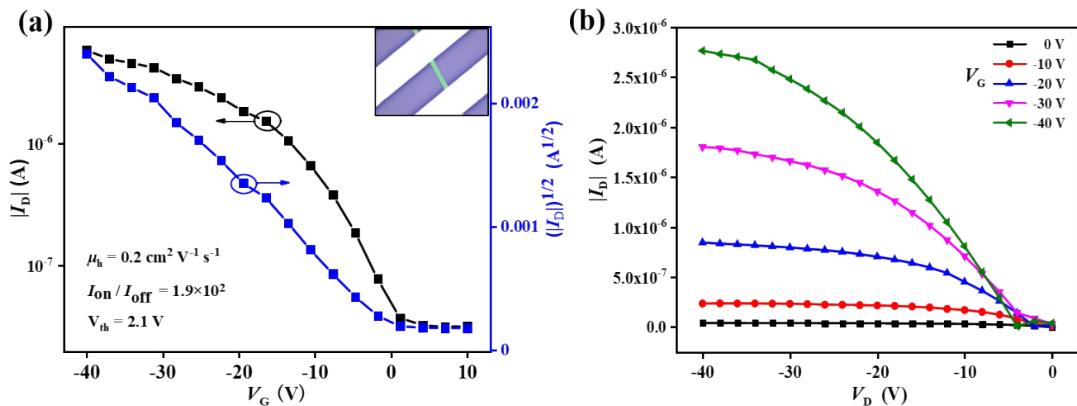
**Figure S3.** Solid-state UV-Vis absorption spectrum of DDCB-TCNQ cocrystal.



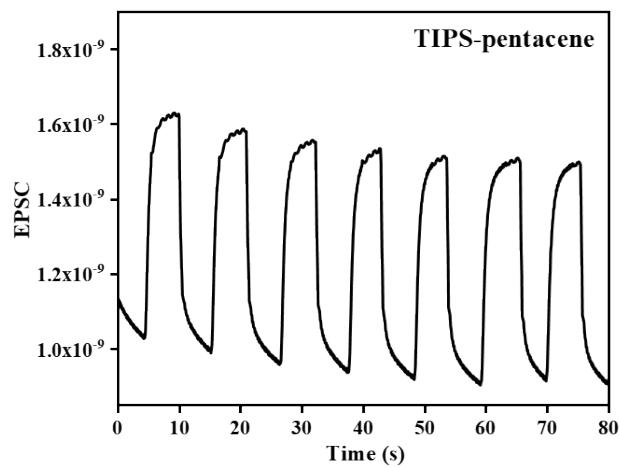
**Figure S4.** IR spectra of DDCB/TCNQ cocrystals.



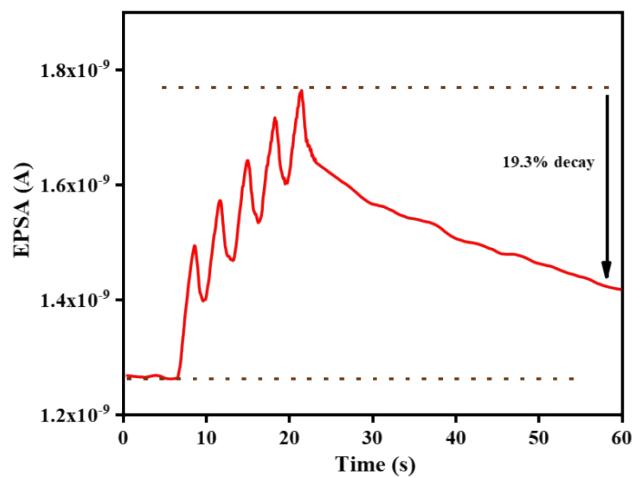
**Figure S5.** Thermogravimetric analysis curve of the DDCB/TCNQ cocrystal.



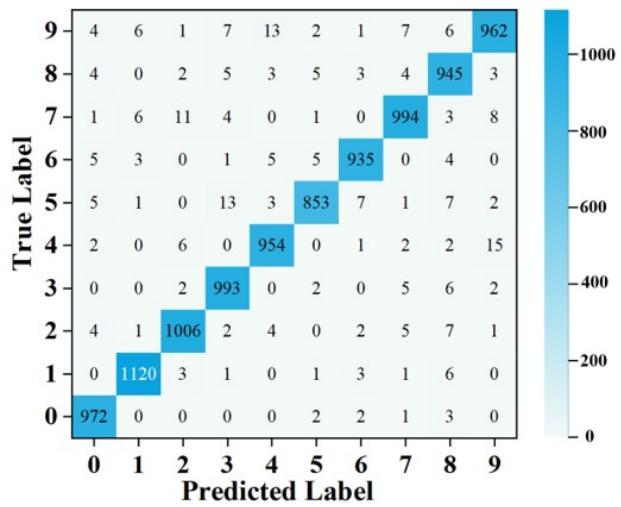
**Figure S6.** (a) Transfer and (b) output curves of TIPS-pentacene microribbon based OFET device.



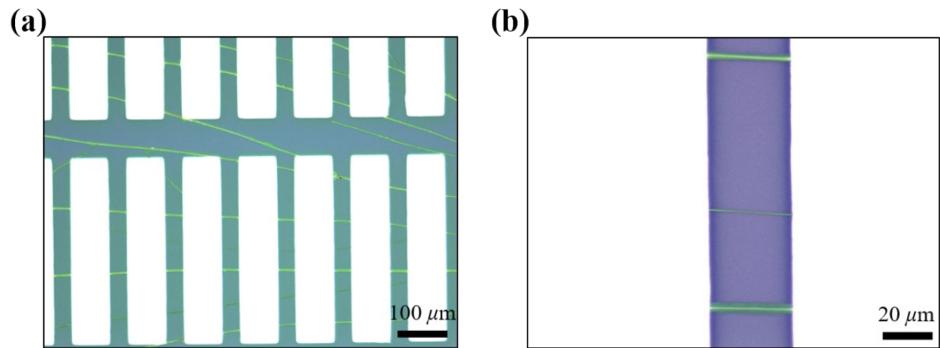
**Figure S7.** Synaptic characteristics of TIPS-pentacene device under light pulse stimulation ( $115.1 \text{ mW/cm}^2$ ,  $V_D = -10 \text{ V}$ ).



**Figure S8.** EPSC of the synaptic transistor triggered by 5 optical pulses (duration: 2 s, intensity:  $115.1 \text{ mW/cm}^2$ ).



**Figure S9.** Confusion matrix after 50 training epochs.



**Figure S10.** (a) Optical microscope images of the synaptic array and (b) magnified view.

**Table S1** Crystal data and structure refinement for DDCB/TCNQ cocrystal.

	DDCB/TCNQ
Formula	C30H16N6
Formula weight	460.49
Temperature (K)	223
Wavelength (Å)	1.54178
Crystal system	monoclinic
space group	<i>P</i> 2 <sub>1</sub> /c
<b>Unit cell dimensions</b> <i>a</i> (Å)	19.6268(9)
<i>b</i> (Å)	6.6292(4)
<i>c</i> (Å)	16.9400(9)
$\alpha$ (°)	90
$\beta$ (°)	95.944(4)
$\gamma$ (°)	90
Volume (Å <sup>3</sup> )	2192.2(2)
<i>Z</i>	4
Absorption coefficient (mm <sup>-1</sup> )	0.683
<i>F</i> (000)	952.0
Crystal size (mm)	0.13 × 0.12 × 0.1
$\theta$ range (°)	9.06 to 136.752
Limiting indices	-23 ≤ <i>h</i> ≤ 23 -7 ≤ <i>k</i> ≤ 7 -20 ≤ <i>l</i> ≤ 17
Reflections collected	16970
<i>R</i> (int)	0.0987
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix leastsquares on <i>F</i> <sup>2</sup>
<i>R</i> [ <i>I</i> > 2sigma( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0573 w <i>R</i> <sub>2</sub> = 0.1344
<i>R</i> (all data)	<i>R</i> <sub>1</sub> = 0.1097 w <i>R</i> <sub>2</sub> = 0.1698
CCDC NO.	2413854