## **Supporting Information**

## Conjugated polymers with deep LUMO levels for field-effect transistors and polymer-polymer solar cells

Andong Zhang,<sup>a</sup> Chengyi Xiao,<sup>a</sup> Dong Meng,<sup>a</sup> Qiang Wang,<sup>b</sup> Xiaotao Zhang,<sup>\*a</sup>

Wenping Hu,<sup>a,c</sup> Xiaowei Zhan,<sup>d</sup> Zhaohui Wang,<sup>\*a</sup> René A. J. Janssen<sup>b</sup> and Weiwei

Li\*a

<sup>a</sup> Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China. E-mail: zhangxt@iccas.ac.cn or wangzhaohui@iccas.ac.cn or liweiwei@iccas.ac.cn

<sup>b</sup> Molecular Materials and Nanosystems, Eindhoven University of Technology P.O. Box 513, 5600 MB Eindhoven, The Netherlands

<sup>c</sup> Collaborative Innovation Center of Chemical Science and Engineering (Tianjin) & Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, China

<sup>d</sup> Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China

The supporting information contains GPC curves of DPP polymers (Fig. S1), absorption spectra of the polymers in chloroform (Fig. S2), cyclic voltammograms of DPP polymers and PCBM (Fig. S3), Output curves of the OFET devices (Fig. S4), Field-effect hole and electron mobility of the DPP polymers thin films without thermal annealing (Table S1), AFM height image of the polymer thin films on Si substrate withoutand with thermal annealing (Fig. S5), and characteristics of PDPP5T:DPP-polymer solar cells fabricated from chloroform with different additives (Table S2).



**Fig. S1** GPC recorded at 140 °C with *o*-DCB as eluent for the thiazole-bridged DPP polymers: (a) PDPP2Tz, (b) PDPP2TzFBDT, (c) PDPP2TzNDI. For PDPP2TzFBDT, only small molecular weight polymer can go through the 0.45  $\mu$ m filter for measurement.



Fig. S2 Optical absorption spectra of the thiazole-bridged DPP polymers in chloroform solution.



**Fig. S3** Cyclic voltammograms of (a) the thiazole-bridged DPP polymers and PDPP5T thin films and (b) [70]PCBM in *o*-DCB. Potential vs.  $Fc/Fc^+$ . LUMO and HOMO of [70]PCBM can be calculated as -4.16 eV and -6.15 eV.



**Fig. S4**. Output curves of the OFET devices fabricated from the polymer thin films under optimized thermal annealing temperature. (a) and (b) PDPP2Tz. (c) and (d) PDPP2TzFBDT. (e) PDPP2TzNDI. (a), (c) for p type, and (b), (d) and (e) for n type.

**Table S1**. Field-effect hole and electron mobility of the DPP polymers thin films without thermal annealing.

Polymer	$\mu_{ m h}$	$\mu_{\rm e}$		
	$(cm^2 V^{-1} s^{-1}) (cm^2 V^{-1} s^{-1})$			
PDPP2Tz	2.44×10-5	2.69×10-3		
PDPP2TzFBDT	-	8.39×10-4		
PDPP2TzNDI	-	5.68×10 <sup>-4</sup>		



**Fig. S5** AFM height image of the polymer thin films on Si substrate without (a, b and c) and with thermal annealing (d, e and f). (a) and (d) PDPP2Tz; (b) and (e) PDPP2TzFBDT; (c) and (f) PDPP2TzNDI. The thermal annealing temperature is 150 °C for PDPP2Tz, 140 °C for PDPP2TzFBDT and 160 °C for PDPP2TzNDI. Root mean square (RMS) surface roughness is 3.13 nm, 0.494 nm, 0.350 nm, 5.04 nm, 0.540 nm and 0.397 nm.

**Table S2.** Characteristics of PDPP5T:DPP-polymer solar cells fabricated from chloroform with different additives. The thickness of active layers is around 70 - 90 nm.

Acceptor	Solvent	$J_{ m sc}$	$V_{\rm oc}$	FF	PCE
		$(mA/cm^2)$	(V)		(%)
PDPP2Tz	CHCl <sub>3</sub>	0.97	0.61	0.35	0.21
	CHCl <sub>3</sub> :DIO 2.5%	0.56	0.57	0.40	0.12
	CHCl <sub>3</sub> :1-CN 3%	1.6	0.57	0.4	0.37
	CHCl3: o-DCB 10%	1.39	0.53	0.37	0.27
PDPP2TzFBDT	CHCl <sub>3</sub>	0.51	0.63	0.36	0.12
	CHCl <sub>3</sub> :DIO 2.5%	0.35	0.61	0.41	0.09
	CHCl <sub>3</sub> :1-CN 3%	0.77	0.61	0.39	0.19

	CHCl <sub>3</sub> :o-DCB 10%	0.51	0.60 0.43 0.13
PDPP2TzNDI	CHCl <sub>3</sub>	0.94	0.54 0.29 0.14
	CHCl <sub>3</sub> :DIO 2.5%	1.87	0.53 0.29 0.29
	CHCl <sub>3</sub> :1-CN 3%	2.2	0.53 0.36 0.42
	CHCl <sub>3</sub> :o-DCB 10%	1.43	0.52 0.31 0.23