### **Electronic Supplementary Information (ESI)**

# Novel conjugated polymers based on bis-dithieno[3,2-b;2',3'-d] pyrrole vinylene donor and diketopyrrolpyrrole acceptor: side chain engineering in organic field effect transistors

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## 1. Analytical Characterization of Materials.



Fig. S1 <sup>1</sup>H NMR Spectra of B(C<sub>12</sub>-DTP)V



Fig. S2  $^{13}$ C NMR Spectra of B(C<sub>12</sub>-DTP)V



Fig. S3 Mass Spectra of B(C<sub>12</sub>-DTP)V

2. Characterization of PB(C<sub>12</sub>DTP)V-DTDPP-C<sub>12</sub> and PB(C<sub>12</sub>DTP)V-DTDPP-C<sub>12</sub>C<sub>8</sub>.



#### 2.1 Thermalgravimetric Analysis (TGA)

**Fig. S4** Thermogravimetric analysis of  $PB(C_{12}DTP)V$ -DTDPP-C<sub>12</sub> and  $PB(C_{12}DTP)V$ -DTDPP-C<sub>12</sub>C<sub>8</sub> at a ramping rate of 10 °C min<sup>-1</sup>.

### 2.2 Differential Scanning Calorimetry (DSC)



**Fig. S5** DSC thermograms of  $PB(C_{12}DTP)V$ -DTDPP- $C_{12}$  and  $PB(C_{12}DTP)V$ -DTDPP- $C_{12}C_8$  polymers.

#### 2.3 AFM analysis



**Fig. S6** Tapping-mode AFM phase images of (a, b)  $PB(C_{12}DTP)V$ -DTDPP-C<sub>12</sub> film after annealing at 220 °C and (c, d)  $PB(C_{12}DTP)V$ -DTDPP-C<sub>12</sub>C<sub>8</sub> film after annealing at 180 °C. Thin film was fabricated by 1,2-dichlorobenzene with spin rate 2000 rpm.



**Fig. S7** Tapping-mode AFM height images of (a, b)  $PB(C_{12}DTP)V$ -DTDPP-C<sub>12</sub> film after annealing at 220 °C and (c, d)  $PB(C_{12}DTP)V$ -DTDPP-C<sub>12</sub>C<sub>8</sub> film after annealing at 180 °C.  $PB(C_{12}DTP)V$ -DTDPP-C<sub>12</sub> film was fabricated by (a) chlorobenzene with spin rate 2500 rpm (R<sub>t</sub> = 2.49 nm), and (b) 1,2-dichlorobenzene with spin rate 1500 rpm (R<sub>t</sub> = 4.17 nm).  $PB(C_{12}DTP)V$ -DTDPP-C<sub>12</sub>C<sub>8</sub> film was fabricated by (c) chlorobenzene with spin rate 2500 rpm (R<sub>t</sub> = 1.64 nm), and (d)1,2-dichlorobenzene with spin rate 1500 rpm (R<sub>t</sub> = 2.66 nm).

#### 2.4 GIXD measurements



**Fig. S8** 2D GIXD pattern of (a) the OCSC  $PB(C_{12}DTP)V$ -DTDPP- $C_{12}$ , (b) the OCSC  $PB(C_{12}DTP)V$ -DTDPP- $C_{12}C_8$ , (c) the spin-coated  $PB(C_{12}DTP)V$ -DTDPP- $C_{12}$  and (d) the spin-coated  $PB(C_{12}DTP)V$ -DTDPP- $C_{12}C_8$  films.



**Fig. S9** In-plane profiles (dot) and Gaussian fitting peaks (color lines), (a) for the OCSC  $PB(C_{12}DTP)V$ -DTDPP-C<sub>12</sub>, and (b) for the OCSC  $PB(C_{12}DTP)V$ -DTDPP-C<sub>12</sub>C<sub>8</sub> films.

#### **2.5 OTFT device performances**

Polymers	Solvent	Spin rate	Coating	T.	Uh adv	V <sub>th</sub>	/ _o#
,		-	direction	- d	$(\mu_{h, max})$	c	-010 -011
		(rpm)		(°C)ª	(cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ) <sup>b</sup>	(V)	
PB(DTP)V- DTDPP-C <sub>12</sub>	ODCB	2000	parallel	RT	0.073	-22	10 <sup>1</sup> -10 <sup>2</sup>
					(0.086)		
	ODCB	2000	parallel	50	0.092	-24	10 <sup>1</sup> -10 <sup>2</sup>
	0000	2000		240	(0.10)	22	4.01 4.02
	ODCB	2000	parallel	240	0.008	-22	$10^{1} - 10^{2}$
		1500	narallol	220	(0.011)	12	101 102
	ODCB	1300	parallel	220	(0.16)	-12	10 -10
	CB	2500	parallel	220	0.13	-29	10 <sup>1</sup> -10 <sup>2</sup>
	00	2000	puraner		(0.19)		10 10
	СВ	2000	parallel	220	0.051	-15	10 <sup>1</sup> -10 <sup>2</sup>
			•		(0.064)		
PB(DTP)V- DTDPP-C <sub>12</sub> C <sub>8</sub>	ODCB	2000	parallel	RT	0.098	-18	10 <sup>1</sup> -10 <sup>2</sup>
					(0.11)		1
	ODCB	2000	parallel	50	0.13	-25	10 <sup>1</sup> -10 <sup>2</sup>
		1500		100	(0.26)	24	101 102
	ODCB	1500	parallel	180	0.55	-21	1010-
	CB	2500	narallel	180	(0.76)	-20	10 <sup>1</sup> -10 <sup>2</sup>
	CD	2300	parallel	100	(0.24)	-20	TO -TO
	СВ	2000	parallel	180	0.062	-32	10 <sup>1</sup> -10 <sup>2</sup>
			1		(0.083)		

**Table S1.** Off-centre spin coated OTFT device performances for B(DTP)V-DTDPP polymers measured under nitrogen

<sup>a</sup>Ta indicates annealing temperature. <sup>b</sup>Average mobilities and maximum values of hole mobility are shown in parentheses (more than 20 devices were tested for each polymer). <sup>c</sup>Averaged vale of 20 devices. ODCB and CB indicate 1,2-dichlorobenzene and chlorobenzene, respectively.