Electronic Supplementary information (ESI):

Influential effect of π-spacers, alkyl side chains, and of the various processing conditions on the photovoltaic properties of alkylselenyl substituted benzodithiophene based polymers Kakaraparthi Kranthiraja,^{‡a} Kumarasamy Gunasekar, ^{‡a} Woosum Cho,^a Young Geun Park,^b Jin Yong Lee,^b Yurim Shin,^c In-Nam Kang,^c Myungkwan Song,^d Keun Hwa Chae,^e BongSoo Kim,^e and Sung-Ho Jin^{*a}

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Fig. S1 ¹H NMR and ¹³C NMR spectra of 2,6-bis(trimethyltin)-4,8-bis(5-2ethylhexyl)selenophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (3a).



hexyldecyl)selenophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (3b).



Fig. S3 ¹H NMR spectrum of P1.



Fig. S4 ¹H NMR spectrum of P2.



Fig. S5 ¹H NMR spectrum of P3.



Fig. S6 ¹H NMR spectrum of P4.



Fig. S7 TGA curves of P1-P4.



Fig. S8 Cyclic voltammograms of P1-P4.





Fig. S9 DFT calculated HOMO and LUMO wave functions of geometry optimized repeating units of **P1-P4**.



Fig. S10 Transfer characteristics of OTFTs based on devices P1-P4.



Fig. S11 X-ray diffraction pattern of P1-P4 films.

Polymer	$M_{\rm w}{}^a$ (g/mol)	$M_{\rm n}{}^a$ (g/mol)	PDI	$T_d(^{o}C)^b$
P1	82000	46000	1.78	342
P2	97000	45000	1.76	334
P3	110000	59000	1.86	342
P4	92000	51000	1.80	340

Table S1. Molecular weights and thermal properties of P1-P4

^{*a*} $M_{\rm w}$, $M_{\rm n}$ and PDI were determined by gel permeation chromatography (GPC) in THF.

^b Decomposition temperature at 5% weight loss.

Polymer	$T_{\text{annealing}}$ (°C)	$\mu_{\rm hole} ({\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})$	$I_{\rm on}/I_{\rm off}$
P1	140	5.5 x 10 ⁻³	1 x 10 ³
P2	140	2.3 x 10 ⁻³	1 x 10 ⁵
Р3	140	7.3 x 10 ⁻³	5 x 10 ²
P4	140	3.1 x 10 ⁻⁴	1 x 10 ²

Table S2. OTFT device characteristics of P1-P4

Table S3. Evaluation of the photovoltaic properties of the OPVs based on polymer: $PC_{71}BM$ 1-chloronapthalene (CN) additive under the illumination of AM 1.5G, 100 mW/cm²

Polymer	Polymer:PC ₇₁ BM	Solvent	$J_{ m sc}$	V _{oc}	FF	РСЕ
	(wt%)		(mA/cm ²)	(V)	(%)	(%)
P1 ^a	1:2	СВ	11.74	0.68	52.97	4.23
P2 ^{<i>a</i>}	1:2	CB	11.50	0.71	57.33	4.69
P3 ^{<i>a</i>}	1:1	CB	12.34	0.68	47.60	4.04
P4 ^{<i>a</i>}	1:1	CB	10.28	0.71	56.76	4.16
^{<i>a</i>} 1 vol% CN was used.						