1 Supplementary Information:

2 Fluorinated low band gap copolymer based on dithienosilole-benzothiadiazole

3 for high-performance photovoltaic device

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17 Figure S1. $M_{\rm w}$ distribution plots of PDTSBT-F (a) and PDTSBT (b), respectively.



Figure S2. (a) TGA curves of PDTSBT-F and PDTSBT under nitrogen atmosphere at a heating
rate of 10 °C min⁻¹. (b) DSC curves of both polymers under nitrogen atmosphere (heating and
cooling rate of 10°C min⁻¹).



Figure S3. J–V characteristics of PDTSBT-F/PC₇₁BM devices (a) different DIO volume (1/1.5
w/w), (b) different D/A ratio (1% DIO) with thermal annealing at 80 °C for 10min, respectively. (c)
different thermal annealed temperature for 10min and (d) different thermal annealed time at 80 °C
(1/1.5 w/w , 1% DIO), respectively.

Condition	Variable	$J_{ m sc}$	V _{oc}	FF	PCE (%)
D/A (w/w) = 1/1.5 DIO/CB (v/v)	0%	7.84	0.72	0.56	3.16
	0.5%	15.67	0.70	0.58	6.36
	1%	15.87	0.70	0.60	6.67
	2%	15.75	0.70	0.60	6.61
DIO/CB (v/v) = 1% D/A (w/w)	1/0.8	15.87	0.72	0.56	6.40
	1/1	15.69	0.72	0.56	6.32
	1/1.5	15.71	0.70	0.60	6.59
	1/2	14.61	0.70	0.61	6.24
D/A (w/w) = 1/1.5 DIO/CB (v/v) = 1% TA temperature	Pristine	15.43	0.70	0.57	6.2
	60 °C	15.49	0.72	0.56	6.24
	80 °C	15.96	0.70	0.60	6.70
	100 °C	15.80	0.70	0.60	6.64
	120 °C	15.49	0.72	0.58	6.47
	140 °C	15.24	0.72	0.55	6.04
D/A (w/w) = 1/1.5 DIO/CB (v/v) = 1% 80 °C	5 min	15.31	0.72	0.57	6.28
	10 min	15.78	0.70	0.60	6.63
	20 min	15.51	0.70	0.60	6.51

32	Table S1. Photovoltaic performance of PDTSBT-F devices under different condition.



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36 Figure S4. AFM of PDTSBT (a, c) and PDTSBT-F (b, d) composite films with PC71BM,

- 37 respectively. Topography images (a-b) and phase images (c-d).
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40 Figure S5. ¹H NMR spectrum of M3 monomer.



43 Figure S6. ¹H NMR spectrum of PDTSBT-F copolymer.



46 Figure S7. ¹H NMR spectrum of PDTSBT copolymer.