SUPPLEMENTARY INFORMATION

Interface design for high-efficiency non-fullerene polymer solar cells

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Table S1. Photovoltaic parameters of solar cells based on PTB7-Th:N2200 BHJ with different interlayers.

	V_{oc}(V)	J_{sc}(mA/cm^2)	FF	PCE(%)	PCE$_{max}$(%)
---	0.69±0.01	13.48±0.21	0.45±0.01	4.2±0.1	4.3
PFN	0.77±0.01	13.18±0.30	0.51±0.02	5.2±0.2	5.4
PFN-2TNDI	0.78±0.01	13.69±0.19	0.58±0.01	6.2±0.1	6.3
Ca	0.78±0.01	12.69±0.29	0.55±0.01	5.4±0.2	5.6

Table S2. Summary of electron mobilities in OFETs.

OFET Mobility (cm^2/Vs)	PC$_{71}$BM-based	N2200-based
Without interface	0.070	0.100
With PFN	0.050	0.009
With PFN-2TNDI	0.025	0.010

(The electron mobility of pure PFN-2TNDI is 1.62×10^{-4} cm^2/Vs.)

Table S3. Photovoltaic parameters of bilayer devices.

Bilayer devices	V_{oc}(V)	J_{sc}(mA/cm^2)	FF	PCE(%)
ITO/PEDOT/PTB7-Th/Al	0.18	0.33	0.26	0.02
ITO/PEDOT/PTB7-Th/PFN(5nm)/Al	0.14	0.34	0.28	0.01
ITO/PEDOT/PTB7-Th/PFN(30nm) /Al	0.01	0.008	0.00	---
ITO/PEDOT/PTB7-Th/PFN-2TNDI(5nm) /Al	0.23	0.39	0.28	0.03
ITO/PEDOT/PTB7-Th/PFN-2TNDI(30nm) /Al	0.81	1.41	0.35	0.40

Table S4. Scanning Kelvin probe microscopy of different WSCPs treated Ag electrodes.

Ag	4.6eV							
Ag/PFN	5nm	4.2eV	10nm	4.2eV	15nm	4.2eV	32nm	4.2eV
Ag/PFN-2TNDI	5nm	4.2eV	11nm	4.1eV	17nm	4.0eV	33nm	3.9eV

Table S5. Photovoltaic parameters of solar cells based on PTB7-Th:IDT-2BR BHJ.

	V_{oc}(V)	J_{sc}(mA/cm^2)	FF	PCE(%)	PCE$_{max}$(%)
---	0.77±0.01	13.49±0.40	0.50±0.01	5.2±0.1	5.3
PFN	1.03±0.01	13.35±0.27	0.51±0.02	7.0±0.2	7.2
PFN-2TNDI	1.04±0.01	13.60±0.35	0.57±0.02	7.9±0.2	8.1
Ca	1.02±0.01	12.67±0.32	0.55±0.02	7.3±0.2	7.5

Table S6. Device parameters of the PSCs based on PTB7-Th:N2200 with different WSCPs in various thicknesses.

WSCP		**V_{oc}(V)**	**J_{sc}(mA/cm^2)**	**FF**	**PCE(%)**	**PCE$_{max}$(%)**
PFN	5nm	0.77±0.01	13.18±0.30	0.51±0.02	5.2±0.2	5.4
	10nm	0.77±0.01	12.76±0.32	0.46±0.01	4.4±0.2	4.6
	15nm	0.64	1.16	0.20	0.15	0.2
	32nm	0.46	0.31	0.23	0.03	0.0
PFN-2TNDI	5nm	0.78±0.01	13.69±0.19	0.58±0.01	6.2±0.1	6.3
	11nm	0.79±0.01	13.46±0.22	0.58±0.01	6.1±0.1	6.2
	17nm	0.78±0.01	13.36±0.31	0.57±0.02	6.1±0.1	6.2
	33nm	0.78±0.01	12.02±0.25	0.58±0.01	5.3±0.2	5.5

Table S7. The EQE curve calculated J_{sc} of the PTB7-Th:N2200 PSCs with different interlayers in various thicknesses under AM 1.5G irradiation (100 mW cm^{-2}).

WSCP	PFN		PFN-2TNDI			
	5nm	10nm	5nm	11nm	17nm	33nm
Calculated J_{sc} (mA cm^{-2})	13.05	12.48	13.60	13.32	13.15	12.10

Table S8. Device parameters of the PSCs based on PTB7-Th:IDT-2BR with PFN-2TNDI as WSCP in various thicknesses.

WSCP		**V_{oc}(V)**	**J_{sc}(mA/cm^2)**	**FF**	**PCE(%)**	**PCE$_{max}$(%)**
PFN-2TNDI	5nm	1.04±0.01	13.60±0.35	0.57±0.02	7.9±0.2	8.1
	11nm	0.89±0.01	13.42±0.40	0.56±0.02	6.4±0.2	6.6
	17nm	0.89±0.01	13.10±0.21	0.55±0.02	6.2±0.1	6.3
	33nm	0.89±0.01	11.69±0.25	0.56±0.01	5.7±0.1	5.8

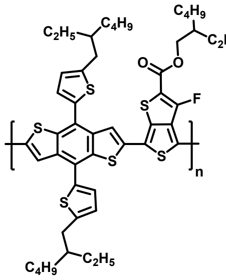
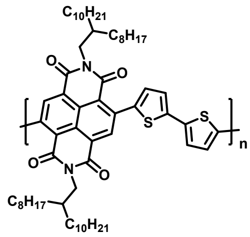
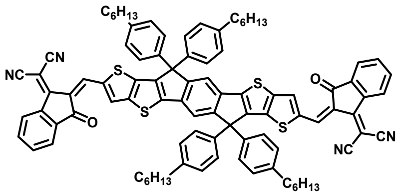
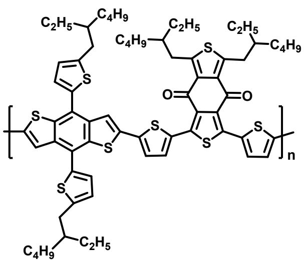
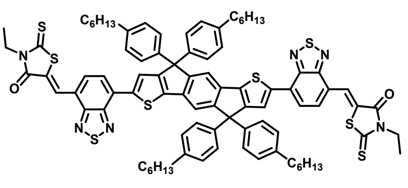
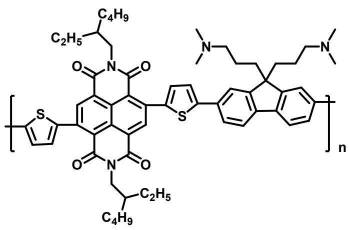
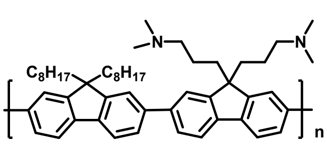
Table S9. The EQE curve calculated J_{sc} of the PTB7-Th: IDT-2BR PSCs with PFN-2TNDI as WSCP in various thicknesses under AM 1.5G irradiation (100 mW cm^{-2}).

WSCP	PFN-2TNDI			
	5nm	11nm	17nm	33nm
Calculated J_{sc} (mA cm^{-2})	13.32	13.12	12.95	11.55

Table S10. The EQE curve calculated J_{sc} of the PBDB-T:ITIC PSCs with PFN-2TNDI as WSCP in various thicknesses under AM 1.5G irradiation (100 mW cm^{-2}).

WSCP	PFN-2TNDI			
	5nm	11nm	17nm	33nm
Calculated J_{sc} (mA cm^{-2})	16.01	15.83	15.54	14.60

Table S11. Related materials and the corresponding original sources.

	**PTB7-Th** purchased from 1-Material Inc**.** Lot No. YY11136
	**N2200** purchased from 1-Material Inc**.** Lot No.YY9286
	**ITIC** purchased from Solarmer Materials Inc. Lot No. KGC23A
	**PBDB-T** synthesized according to the reported procedure (*Macromolecules*, 2012, 45, 9611-9617). M_w=13.5 kDa, PDI=1.18.
	**IDT-2BR** synthesized according to the reported procedure (*Energ. Environ. Sci.*, 2015, 8, 3215-3221) and verified by NMR.
	**PFN-2TNDI** synthesized according to the reported procedure (*J. Am. Chem. Soc.*, 2016, 138, 2004-2013). M_w=21.0 kDa, PDI=1.70.
	**PFN** synthesized according to the reported procedure (*Chem. Mater.* 2004, 16, 708-716). M_w=35.2 kDa, PDI=1.54.

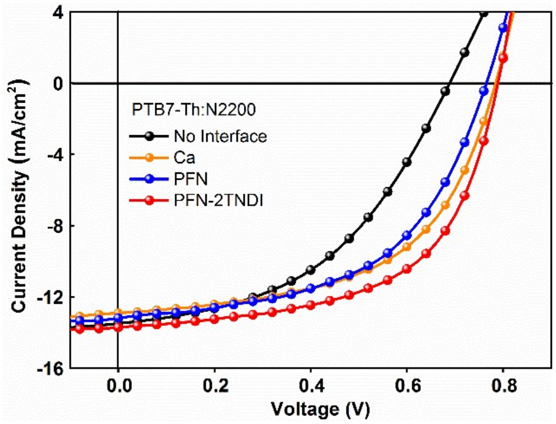


Figure S1. *J-V* curves of best solar cells based on PTB7-Th:N2200 BHJ with different interlayers and simulated AM 1.5G irradiation (100 mW cm^{-2}).

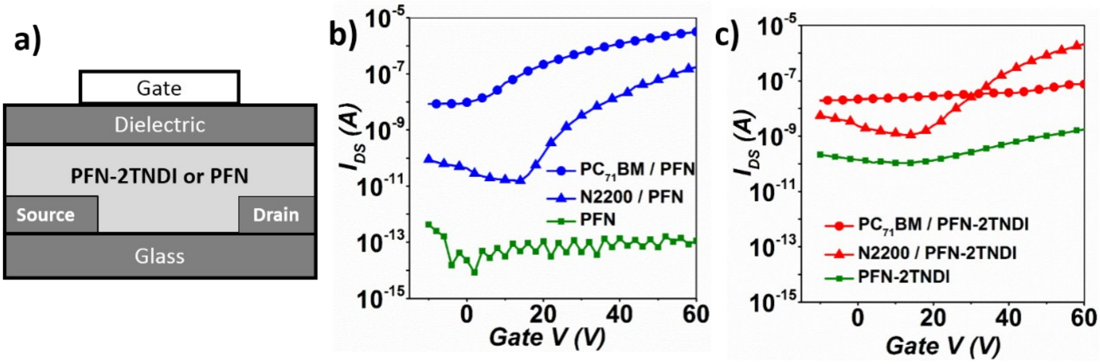


Figure S2. (a) OFET structure of pure interlayer device, and transfer plots of (b) PFN-based and (c) PFN-2TNDI-based monolayer or bilayer structure OFET.

In the case of PFN-based OFET, a very low I_{DS} of ~10^{-14}-10^{-13}A across the whole range of gate bias voltage was measured, indicating that PFN is very insulating in nature. The pure PFN-2TNDI-based OFET shows a much higher I_{DS} of ~10^{-10}-10^{-9} A with a $I_{on/off}$ ratio of ~10, indicating that the PFN-2TNDI is slightly self-doped due to the electron transfer from the amine on the polymer side chain to the π-conjugated backbone as discussed in our previous report. The electron mobilities for all the different OFET devices were also provided in Table S2. As the electron mobility of PCBM (0.07 cm^2/Vs) is over 2 order of magnitudes higher than that of PFN-2TNDI, we postulate that the major charge transport channel is through the PCBM layer and the PFN-2TNDI only plays a relatively small role on the charge transport although the charge transport within the PFN-2TNDI cannot be totally excluded. Both the electron mobilities of the PCBM/PFN and PCBM/PFN-2TNDI were only slightly lower than the pure PCBM film, which also suggested that the major charge transport channel in the bilayer film is in the PCBM layer. The significantly reduced current and mobility of the single interlayer curve compared to the bilayer device were also observed in the N2200-based devices.

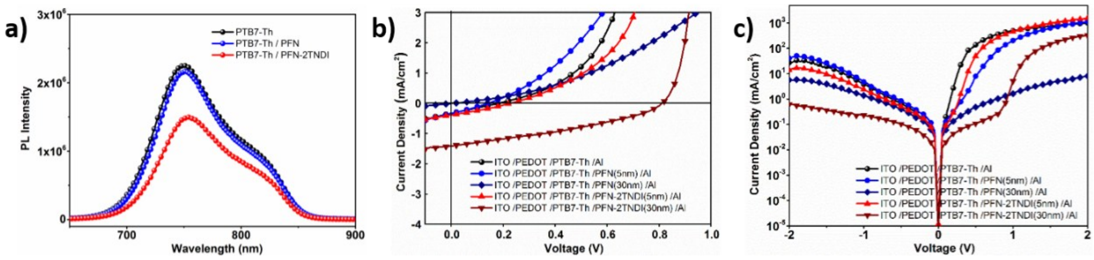


Figure S3. (a) PL spectra of pristine polymer PTB7-Th and its bilayers with PFN or PFN-2TNDI in solid film states, and *J-V* characteristics of bilayer devices (b) under illumination and (c) in dark.

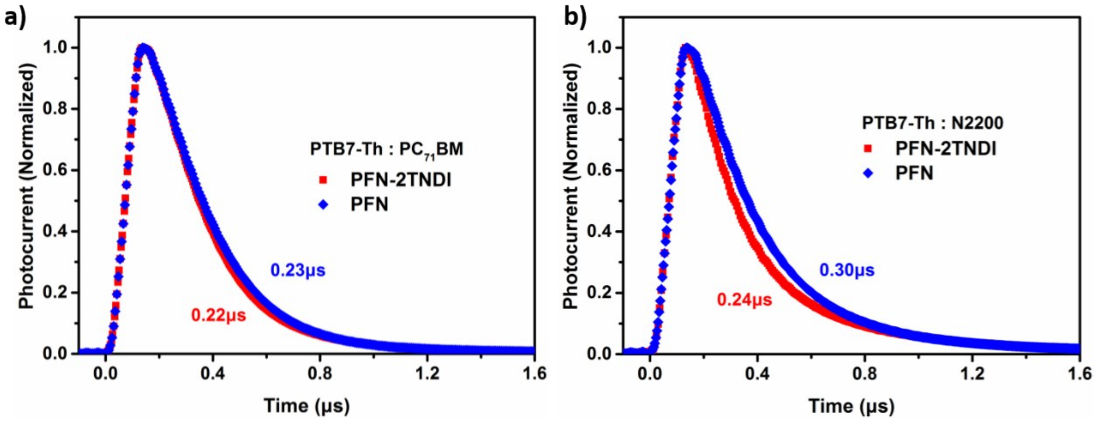


Figure S4. Photocurrent decay determined from devices based on (a) PTB7-Th:$PC_{71}BM$ BHJ, and (b) PTB7-Th:N2200 BHJ with different interlayers.

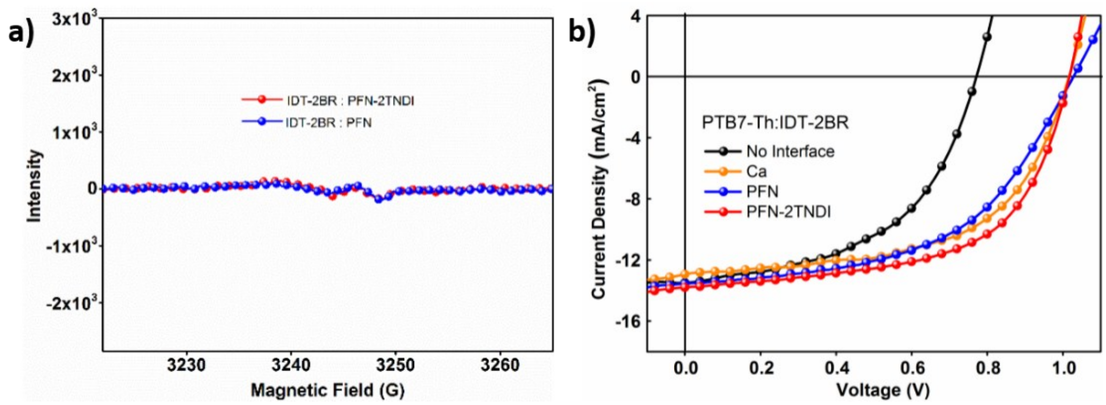


Figure S5. (a) Electron spin resonance of blends based on IDT-2BR in solid states. (b) Device performance of best solar cells based on PTB7-Th:IDT-2BR BHJ with different interlayers.

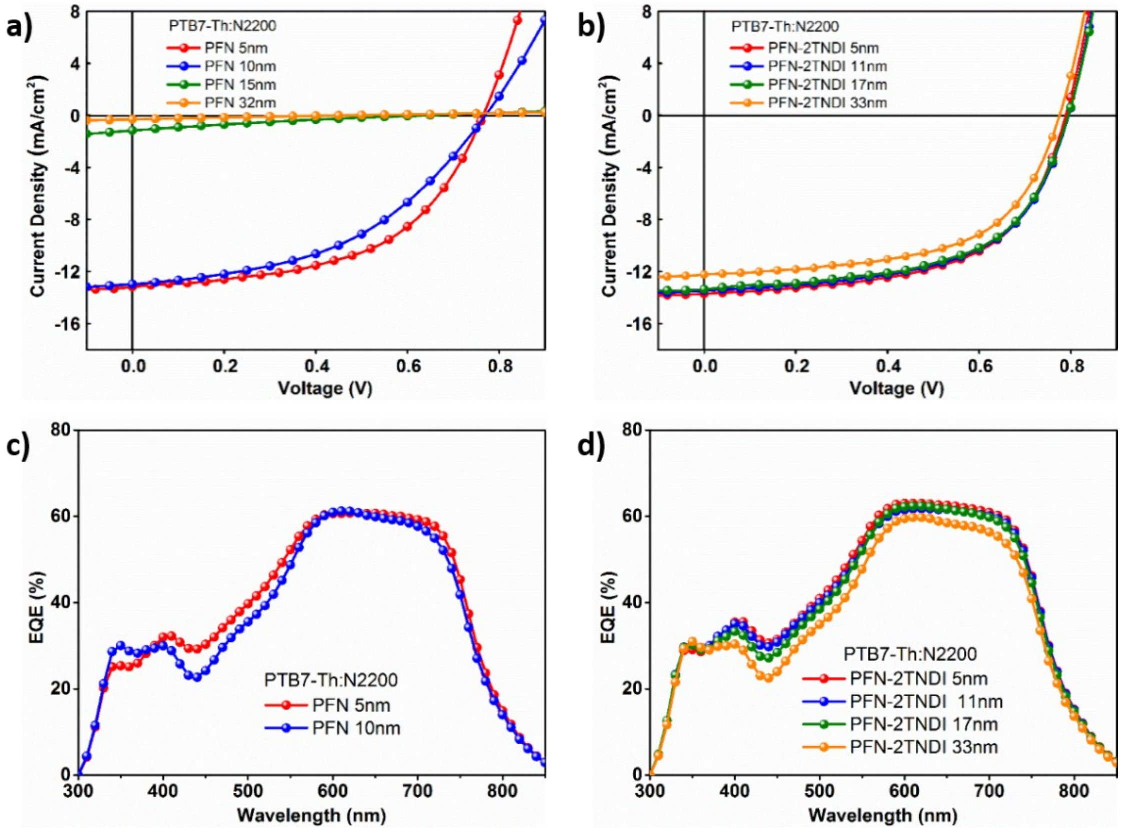


Figure S6. *J-V* curves and EQE spectra of best solar cells based on PTB7-Th:N2200 BHJ with (a,c) PFN, and (b,d) PFN-2TNDI as WSCPs in various thicknesses.

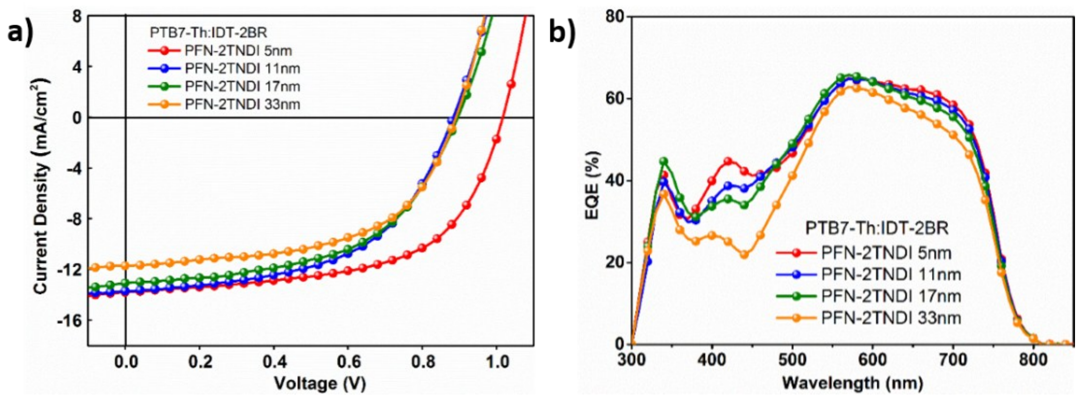


Figure S7. (a) *J-V* curves and (b) EQE spectra of devices based on PTB7-Th:IDT-2BR BHJ with PFN-2TNDI as WSCP in various thicknesses.

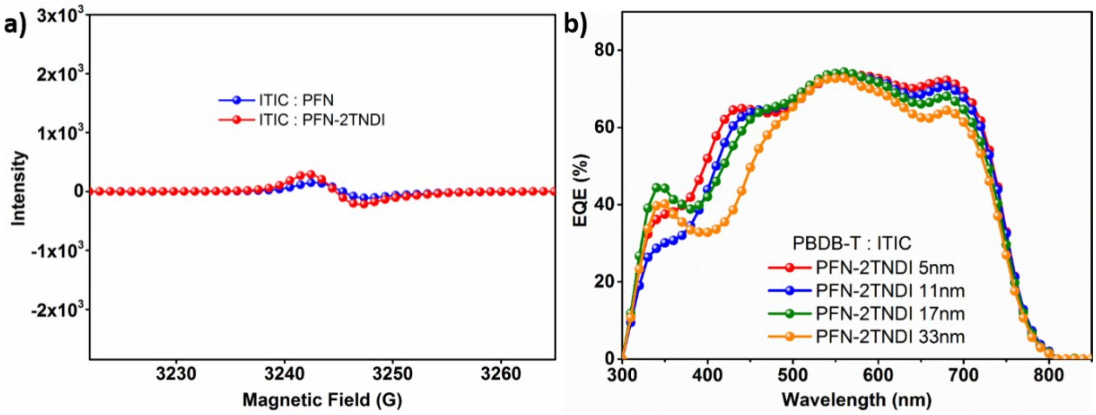


Figure S8. (a) Electron spin resonance of blends based on ITIC in solid states. (b) EQE spectra of devices based on PBDB-T:ITIC BHJ with PFN-2TNDI as WSCP in various thicknesses.

中 国 计 量 科 学 研 究 院

证书编号 GXtc2016-1471
Certificate No.

校 准 结 果
Calibration Results

有效面积 (cm²)	短路电流 I_{sc}(mA)	开路电压 V_{oc}(V)	最大功率 P_{max}(mW)
0.037813	0.61	0.94	0.40

最大功率电流 I_{max}(mA)	最大功率电压 V_{max}(V)	填充因子 FF (%)	转换效率 (PCE) η (%)
0.53	0.76	69.8	10.6

不确定度描述 Uncertainty:
I_{sc} ：1.8%（k=2）； V_{oc}：1.0%（k=2）； P_{max}：2.1%（k=2）。

注 Note:
1. 太阳电池的有效面积为 0.037813cm²（证书编号：CDjc2016-5983）。
The certificated cell area is 0.037813cm² (Certificate No.: CDjc2016-5983).
2. 此数据仅对被测样品当时状态有效。
The data apply only at the time of the test for the sample.

建议 Suggestion:
根据客户要求和测试文件的规定，通常情况下 12 个月校准一次。
According to the client or the test documents, the recommended calibration cycle is 12 months.

声明 Statement:
1.我院仅对加盖“中国计量科学研究院校准专用章”的完整证书负责。
NIM is ONLY responsible for the complete certificate with the calibration stamp of NIM.
2.本证书的测试结果仅对所校准的计量器具有效。
The certificate is ONLY valid for the test ed instrument.
3.本证书用中英文两种语言表达，准确含义以中文为准。
The certificate is reported in both English and Chinese, with the Chinese version as standard.

测 试 员： 核 验 员：

Figure S9. The PCE certification of a PBDB-T:ITIC BHJ based PSC .