Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Supporting Information

PCE11-Based Polymer Solar Cells with High Efficiency over 13% Achieved by Room-Temperature Processing

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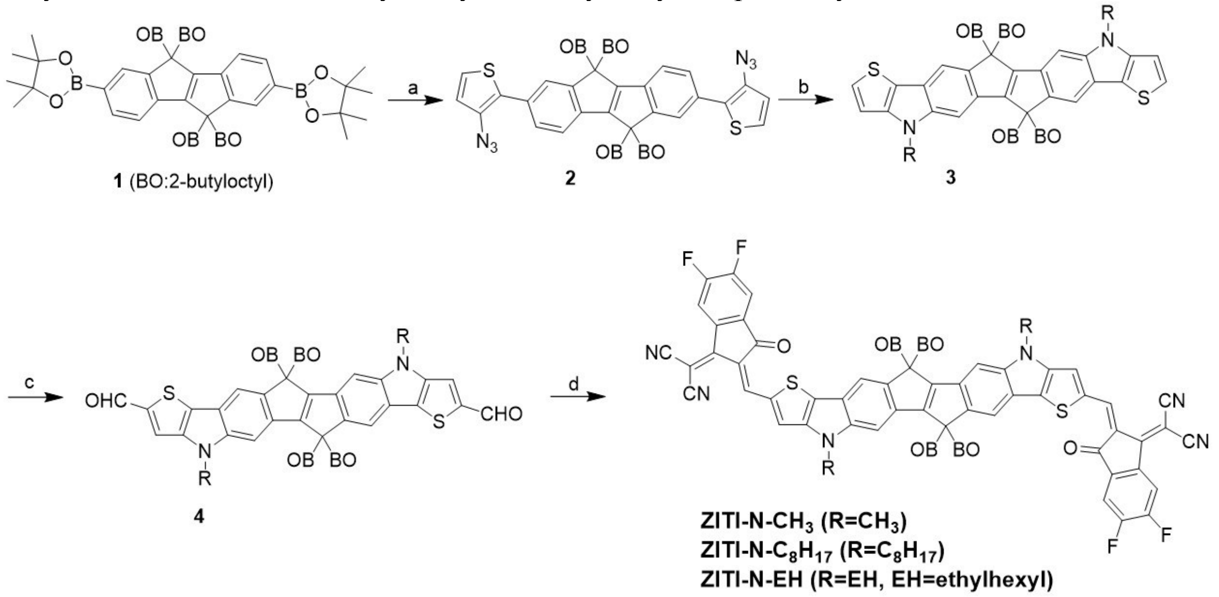
Synthetic Procedures

The synthetic route for compound ZITI-N-R is similar with the synthesis of ZITI-N,[50] the alkylation reaction with methyl, octyl and ethylhexyl, respectively.



Scheme S1. Synthesis of ZITI-N-R NFAs. Reagents and conditions: a, (i) 2,3-Dibromothiophene, $Pd(PPh_3)_4$, THF; (ii) *n*-BuLi, Tos-N_3, THF. b, (i) *o*-dichlorobenzene, 160 °C; (ii) NaH, CH_3I, DMF. c, $POCl_3$, DMF. d, INCN-2F, pyridine, $CHCl_3$.

Compound ZITI-N-C_8H_{17}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.99 (s, 2H), 8.54 (m, 2H), 7.87 (s, 2H), 7.82 (s, 2H), 7.69 (t, ^3J = 7.5 Hz, 2H), 7.26 (s, 2H), 4.29 (m, 4H), 2.17 (m, 8H), 1.94(m, 4H), 1.30-0.50 (m, 118H); HRMS (MALDI-TOF) calcd for $C_{100}H_{118}F_4N_6O_2S_2$ $[M]^+$: 1771.0879, found, 1771.0874.

Compound ZITI-N-EH. ^1H NMR (400 MHz, $CDCl_3$): δ 8.97 (s, 2H), 8.54 (m, 2H), 7.89 (s, 2H), 7.82 (s, 2H), 7.69 (t, ^3J = 7.6 Hz, 2H), 7.30 (s, 2H), 4.18 (m, 4H), 2.13 (m, 10H), 1.20-0.50 (m, 120H); HRMS (MALDI-TOF) calcd for $C_{100}H_{118}F_4N_6O_2S_2$ $[M]^+$: 1771.0879, found, 1771.0871.

ZITI-N-CH_3:
2,2'-[[6,6,13,13-tetrakis(2-butyloctyl)-4,11-dimethyl-4,6,11,13-tetrahydropentaleno[2,1-*f*:5,4-*f*']dithieno[3,2-*b*:3',2'-*b*']diindole-2,9-diyl]bis[methylidyne(5,6-difluoro-3-*oxo*-1*H*-indene-2,1(3*H*)-diylidene)]]bis[malononitrile]

ZITI-N-C_8H_{17}:
2,2'-[[6,6,13,13-tetrakis(2-butyloctyl)-4,11-dioctyl-4,6,11,13-tetrahydropentaleno[2,1-*f*:5,4-*f*']dithieno[3,2-*b*:3',2'-*b*']diindole-2,9-diyl]bis[methylidyne(5,6-difluoro-3-*oxo*-1*H*-indene-2,1(3*H*)-diylidene)]]bis[malononitrile]

ZITI-N-EH:
2,2'-[[6,6,13,13-tetrakis(2-butyloctyl)-4,11-2-ethylhexyl-4,6,11,13-tetrahydropentaleno [2,1-*f*:5,4-*f'*]dithieno[3,2-*b*:3',2'-*b*']diindole-2,9-diyl]bis[methylidyne(5,6-difluoro-3-*oxo*-1*H*-indene-2,1(3*H*)-diylidene)]]bis[malononitrile]

The preparation of ZnO sol-gel is based on the reference (*Adv. Mater.,* 2013, **25**, 2397–2402). The detail process is shown below:
Zinc acetate dihydrate [$Zn(CH_3COO){\bullet}2H_2O$] (Aldrich, 99.9%) with 0.1 M concentration was first dissolved in anhydrous ethanol [CH_3CH_2OH] (99.5+% Aldrich) and rigorously stirred for 2–3 h at 80 °C. Subsequently, ethanolamine was added to the solution as sol stabilizer followed by thorough mixing process with magnetic stirrer for 12-15 h at 60 °C.

The measurement of film thickness. The step profiler was used to measure the film thickness by scanning profilometry. A thin probe was used to scan the surface of the sample. When a height difference was detected, the changes was converted into voltage signal in the internal circuit and then the film thickness was calculated.

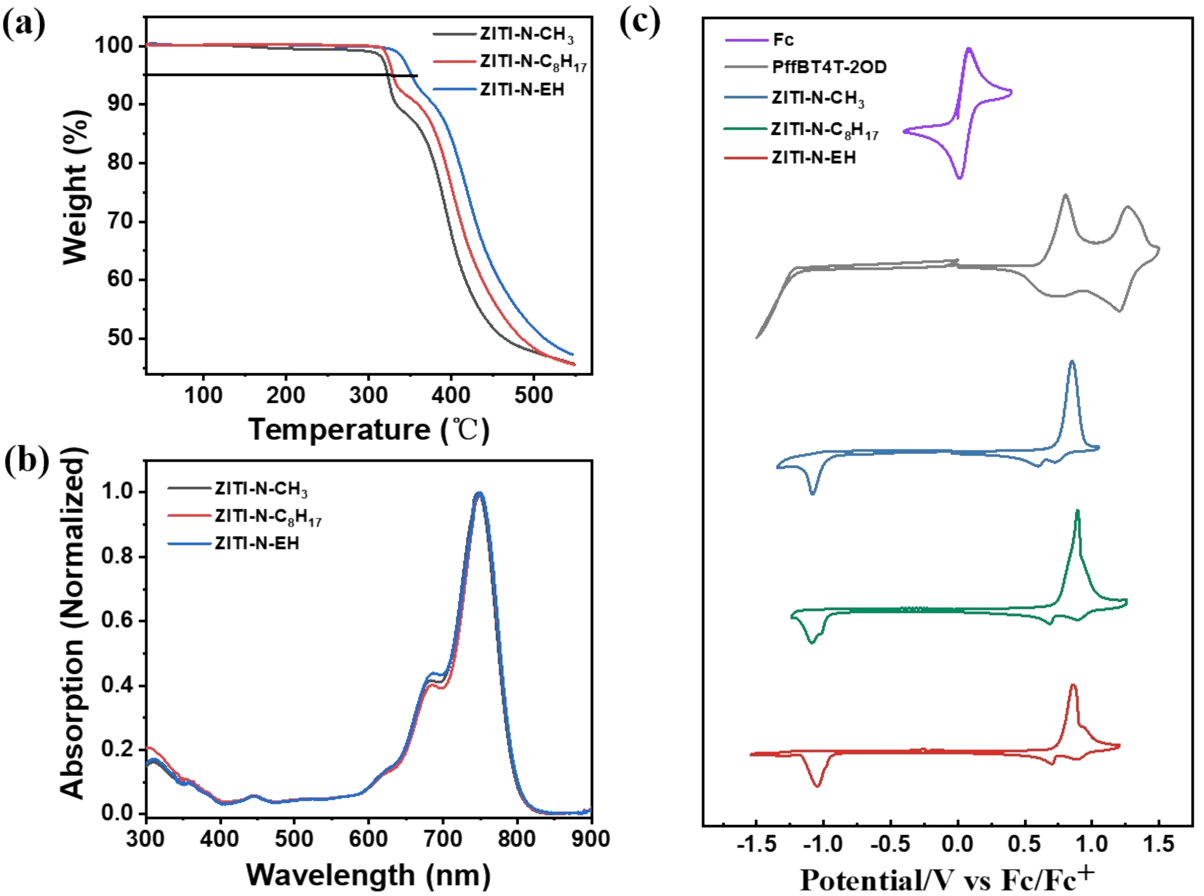


Fig. S1 (a) Thermal gravimetric analysis (TGA) curve of ZITI-N-CH_3, ZITI-N-C_8H_{17} and ZITI-N-EH; (b) UV-vis-NIR absorption spectra of ZITI-N-CH_3, ZITI-N-C_8H_{17} and ZITI-N-EH in chloroform; (c) Cyclic voltammogram of PffBT4T-2OD, ZITI-N-CH_3, ZITI-N-C_8H_{17} and ZITI-N-EH films in 0.1 mol/L CH_3CN solution of tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte with a scan rate of 100 mV s^{-1}.

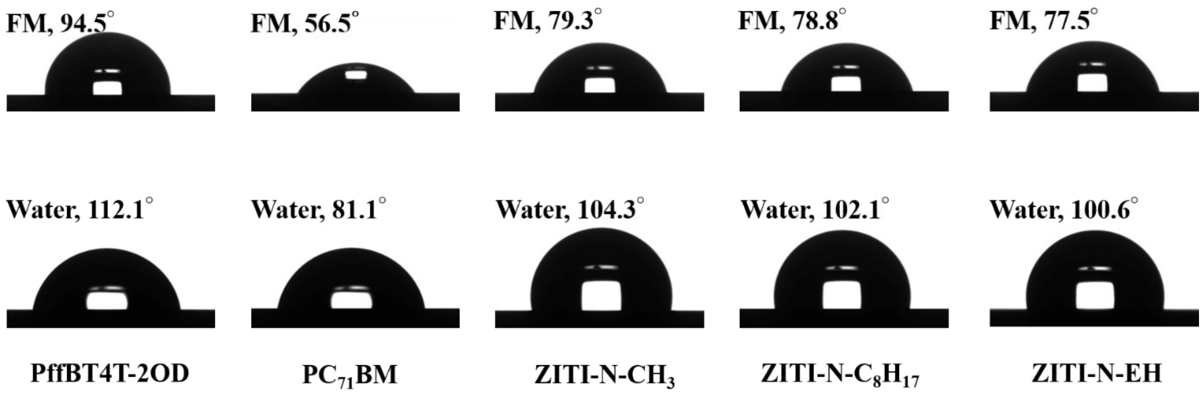


Fig. S2 Contact angles of formamide (FM) and water droplets on PffBT4T-2OD, $PC_{71}BM$, ZITI-N-CH_3, ZITI-N-C_8H_{17}, and ZITI-N-EH neat films.

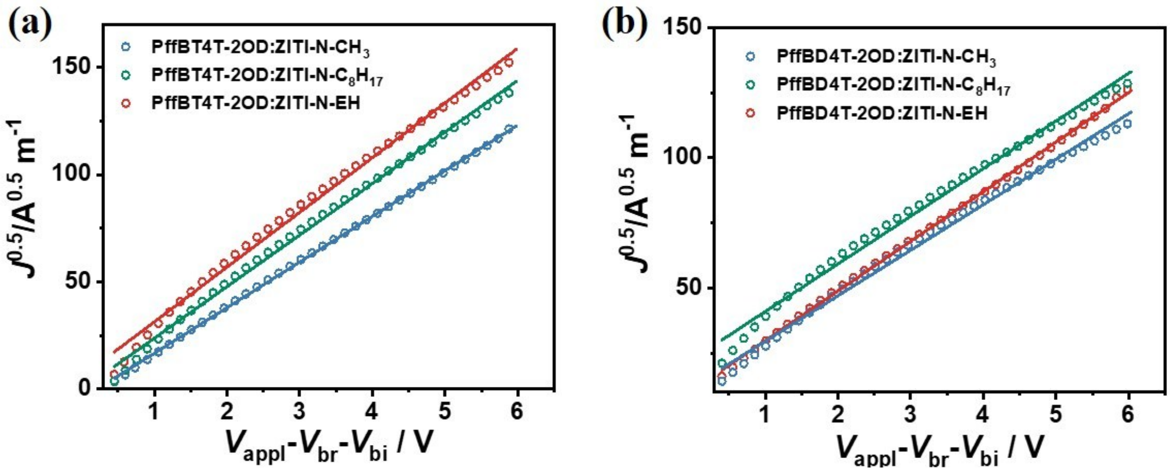


Fig. S3 $J^{0.5}$ *vs* V characteristics for PffBT4T-2OD:ZITI-N-CH_3-, PffBT4T-2OD:ZITI-N-C_8H_{17}- and PffBT4T-2OD:ZITI-N-EH-based PSCs; hole-only diode (a) and electron-only diode (b).

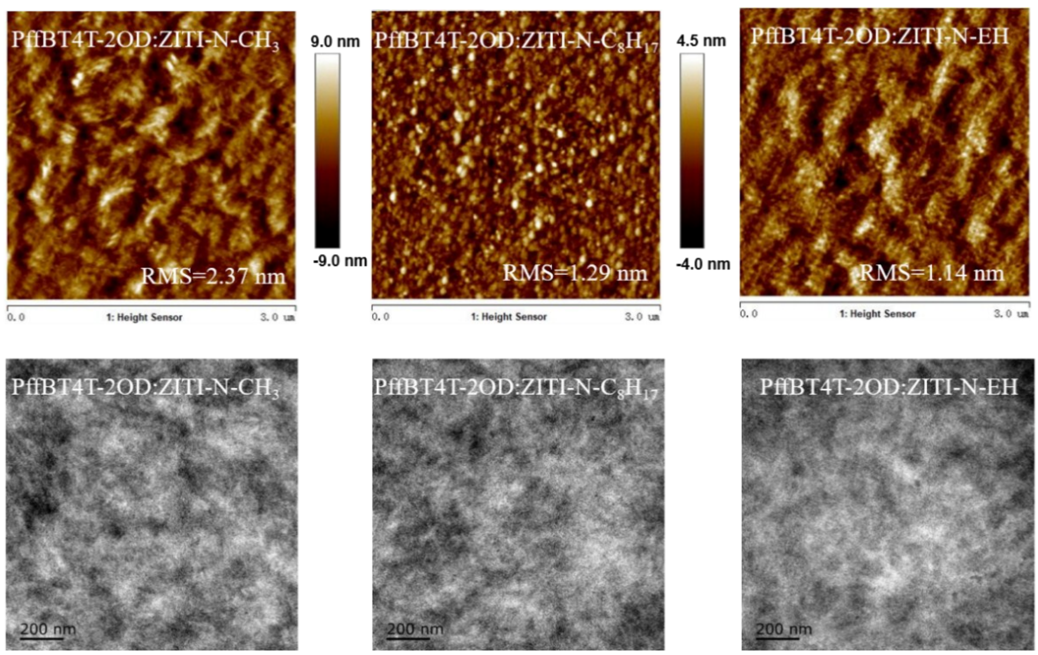


Fig. S4 AFM height images (up) and TEM (down) images of the PffBT4T-2OD:ZITI-N-CH_3, PffBT4T-2OD:ZITI-N-C_8H_{17} and PffBT4T-2OD:ZITI-N-EH blend films.

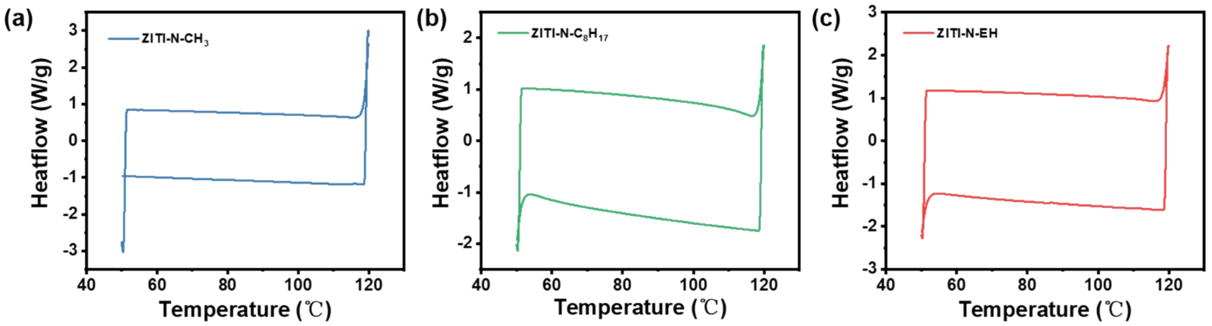


Fig. S5. Differential scanning calorimetry (DSC) curves of ZITI-N-CH_3, ZITI-N-C_8H_{17}, and ZITI-N-EH with a heating rate of 10 °C min^{-1} under inert atmosphere.

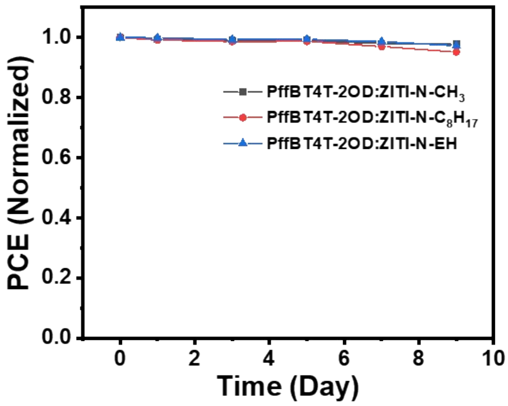


Fig. S6. The evolution of the photovoltaic performance over storage time of the optimized device based on the PffBT4T-2OD:ZITI-N-R (R=CH_3, C_8H_{17}, EH) with encapsulation in glove box.

Table S1. The contact angles and surface energy parameters of the materials.

Organic layer	Contact angle water [deg]	Contact angle FM[(a)] [deg]	γ_d [(b)] [mN m^{-1}]	γ_p [(b)] [mN m^{-1}]	γ [mN m^{-1}]	$(\sqrt{\gamma_{donor}}-\sqrt{\gamma_{accept}}$ [(c)]
PffBT4T-2OD	112.1	94.5	16.19	2.21	18.40	--
$PC_{71}BM$	81.1	56.5	25.77	10.64	36.41	3.04
ZITI-N-CH_3	104.3	79.3	25.13	2.12	27.25	0.87
ZITI-N-C_8H_{17}	102.1	78.8	23.27	3.34	26.61	0.76
ZITI-N-EH	100.6	77.5	22.21	4.17	26.38	0.72

(a) FM is formamide; (b) γ_d and γ_p represent the surface free energies generated from the dispersion forces and the polar forces, respectively; (c)Estimates for all Flory-Huggins interaction parameter ($\chi_{donor,acceptor}$) can in principle be derived using the relation of $\chi_{donor,acceptor} = K(\sqrt{\gamma_{donor}} - \sqrt{\gamma_{acceptor}})^2$ (K is a constant)[51]

Table S2. Photovoltaic performance of PffBT4T-2OD:ZITI-N-R-based solar cells with different D/A ratio. Average values with standard deviation were obtained from 6 devices.

	D:A	V_{oc} (V)	J_{sc} (mA cm^{-2})	**FF** (%)	**PCE** (%)
PffBT4T-2OD:ZITI-N-CH_3	1:0.8	0.827	17.51	59.48	8.61 (8.39±0.24)
	1:1	0.824	18.97	56.02	8.78 (8.52±0.22)

	1:1.2	0.825	19.12	52.34	8.26 (8.10±0.20)
PffBT4T-2OD:ZITI-N-C_8H_{17}	1:0.8	0.801	20.76	71.19	11.83 (11.66±0.19)
	1:1	0.802	21.04	71.85	12.13 (11.92±0.14)
	1:1.2	0.790	20.32	68.55	11.01 (10.78±0.14)
PffBT4T-2OD:ZITI-N-EH	1:0.8	0.813	20.83	73.22	12.42 (12.18±0.18)
	1:1	0.805	22.13	73.35	13.07 (12.80±0.15)
	1:1.2	0.801	21.67	67.63	11.70 (11.44±0.21)

Table S3. Photovoltaic performance of PffBT4T-2OD:ZITI-N-R-based solar cells different thermal annealing temperature. Average values with standard deviation were obtained from 6 devices.

	Treatment	V_{oc} (V)	J_{sc} (mA cm^{-2})	**FF** (%)	**PCE** (%)
PffBT4T-2OD:ZITI-N-CH_3	as-cast	0.837	17.60	50.93	7.51 (7.36±0.16)
	80°C/10 min	0.826	18.74	52.87	8.18 (7.94±0.28)
	100°C/10 min	0.824	18.97	56.02	8.78 (8.52±0.22)
	120°C/10 min	0.818	19.29	52.03	8.22 (8.01±0.27)
PffBT4T-2OD:ZITI-N-C_8H_{17}	as-cast	0.813	20.38	66.78	11.05 (10.79±0.15)
	80°C/10 min	0.812	20.76	71.19	11.98 (11.80±0.12)
	100°C/10 min	0.802	21.04	71.85	12.13 (11.92±0.14)
	120°C/10 min	0.801	20.39	72.81	11.89 (11.73±0.19)
PffBT4T-2OD:ZITI-N-EH	as-cast	0.817	20.77	70.32	11.94 (11.76±0.15)
	60°C/10 min	0.812	21.28	69.80	12.56 (12.48±0.19)
	80°C/10 min	0.805	22.13	73.35	13.07 (12.80±0.15)
	100°C/10 min	0.795	21.69	69.50	12.01 (11.77±0.26)

Table S4. Photovoltaic performance of PffBT4T-2OD:ZITI-N-R-based solar cells with different thicknesses. Average values with standard deviation were obtained from 6 devices.

	rpm	**Thickness** (nm)	V_{oc} (V)	J_{sc} (mA cm^{-2})	**FF** (%)	**PCE** (%)
PffBT4T-2OD:ZITI-N-CH_3	3500r	110 nm	0.824	18.78	55.04	8.52 (8.27±0.19)
	3000r	130 nm	0.824	18.97	56.02	8.78 (8.52±0.22)
	2500r	170 nm	0.820	19.53	47.71	7.64 (7.41±0.13)
	2000r	200 nm	0.819	19.35	45.21	7.16 (7.05±0.18)
PffBT4T-2OD:ZITI-N-C_8H_{17}	3500r	110 nm	0.801	20.39	72.81	11.89 (11.76±0.16)
	3000r	130 nm	0.802	21.04	71.85	12.13 (11.92±0.14)
	2500r	170 nm	0.798	21.01	68.82	11.51 (11.34±0.14)
	2000r	200 nm	0.797	20.98	66.12	11.04 (10.74±0.24)
PffBT4T-2OD:ZITI-N-EH	3500r	110 nm	0.806	21.74	71.93	12.62 (12.47±0.24)
	3000r	130 nm	0.805	22.13	73.35	13.07 (12.80±0.15)
	2500r	170 nm	0.804	22.12	70.30	12.57 (12.43±0.10)
	2000r	200 nm	0.804	22.45	67.79	12.35 (12.14±0.13)

Table S5. The photovoltaic parameters of TDA polymer-based PSCs.

Active layer	Processing temperature (℃)	Thickness (nm)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	Ref.
PNTDT-2F2T:$PC_{71}BM$	40	210	0.73	18.80	70.0	9.63	1
NT812:$PC_{71}BM$	70	300	0.72	20.61	66.99	10.2	2
PffBTT_2-DPPT_2 $PC_{71}BM$	100	100	0.81	17.26	60	8.44	3
PTBTz-2:$PC_{71}BM$	100	100	0.83	16.84	69.5	9.72	4
PffBT4T-2OD:$PC_{71}BM$	110	240	0.76	17.8	61	8.3	5
PffBT4T-2OD:$PC_{71}BM$	100	300	0.79	18.5	71	10.3	5
PffBT4T-2OD:$PC_{71}BM$	80	350	0.76	17.3	60	7.9	5
PffBX4T-2DT:$PC_{71}BM$	110	250	0.875	15.8	66	9.4	6
PffBX4T-2DT:$PC_{71}BM$	110	110	0.878	13.6	72	8.9	6
PffBX4T-2DT:$PC_{71}BM$	110	300	0.867	15.9	62	8.7	6
PffBT-T3(1,2)-2:$PC_{71}BM$	110	250	0.82	18.7	68.3	10.5	7
P3:$PC_{71}BM$	110	210	0.66	20.69	71	9.76	8
P2:$PC_{71}BM$	110	136	0.69	16.3	69	7.76	9
PffBT4T-2OD:$PC_{71}BM$	110	300	0.77	18.4	74	10.5	10
PBDTTT-H:$PC_{71}BM$	110	95	0.8	17.37	67.5	9.38	11
PNTz4TF2:$PC_{71}BM$	160	230	0.82	19.3	0.67	10.5	11
PffT2-FTAZ:$PC_{71}BM$	115	250	0.8	13.3	69	7.5	12
FBT-Th4(1,4):$PC_{71}BM$	60	230	0.76	16.2	62.1	7.64	13
PffBT-2TPF4-19/1:$PC_{61}BM$	30	169	0.754	17.05	69.3	8.9	14
PffBT-2TPF4-9/1:$PC_{61}BM$	30	168	0.769	17.18	70.8	9.4	14
PffBT-2TPF4-4/1:$PC_{61}BM$	30	148	0.772	16.55	72.7	9.3	14
PffBT4T90-co-3T10:$PC_{71}BM$	25	400	0.73	19.9	65.0	9.6	15
PffBT4T-2OD:BTR:$PC_{71}BM$	25	300	0.77	18.28	74.02	10.59	16
PNTT:BTR:$PC_{71}BM$	25	300	0.77	20.83	70.43	11.44	16
PffBX-TT:$PC_{71}BM$	130	250	0.85	15.3	66.2	9.10	17
PffBX-DTT:$PC_{71}BM$	25	260	0.82	12.8	62.2	6.66	17
PFBT4T-C5Si-25%:$PC_{71}BM$	90	420	0.76	19.08	74.12	11.09	18
PTFB-O:ITIC-Th	110	96	0.92	16.70	67.6	10.9	19
PffBT4T-2DT:EH-IDTBR	60	80	1.02	17.2	0.63	11.1	20
PffBT4T-2OD:BAF-4CN	70	290	0.769	15.52	70.7	8.4	21
PffT2-FTAZ-2DT:IEIC	80	80	0.998	12.2	59	7.2	22
P3TEA:SF-PDI_2	90	120	1.11	13.27	64.3	9.5	23
PTP8:P(NDI2HD-Se)	135	133	0.99	9.7	62.6	6.01	24
PffBT4T-2OD:EH-IDTBR	110	300	1.03	16.1	54.5	9.1	25
PffBT4T-2OD:ZITI-N-EH	25	130	0.805	22.13	73.35	13.07	This work

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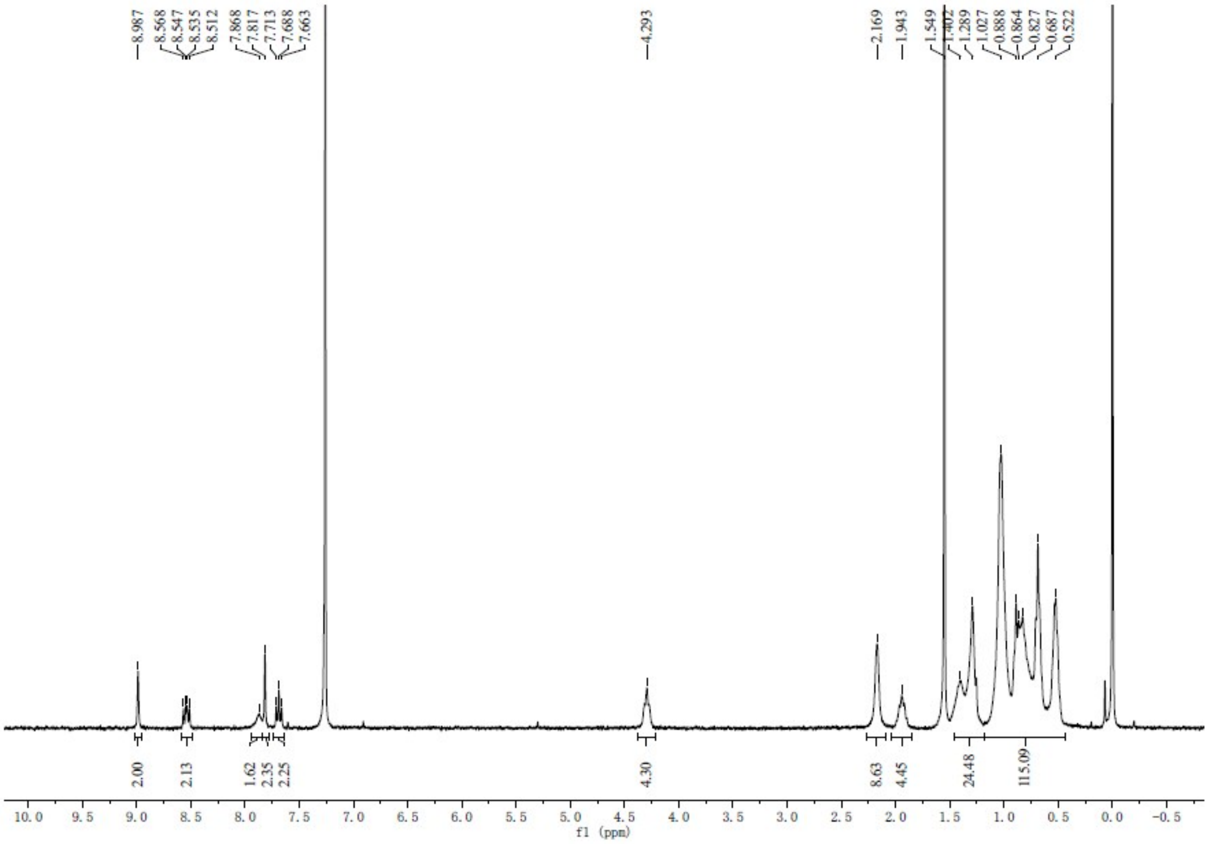
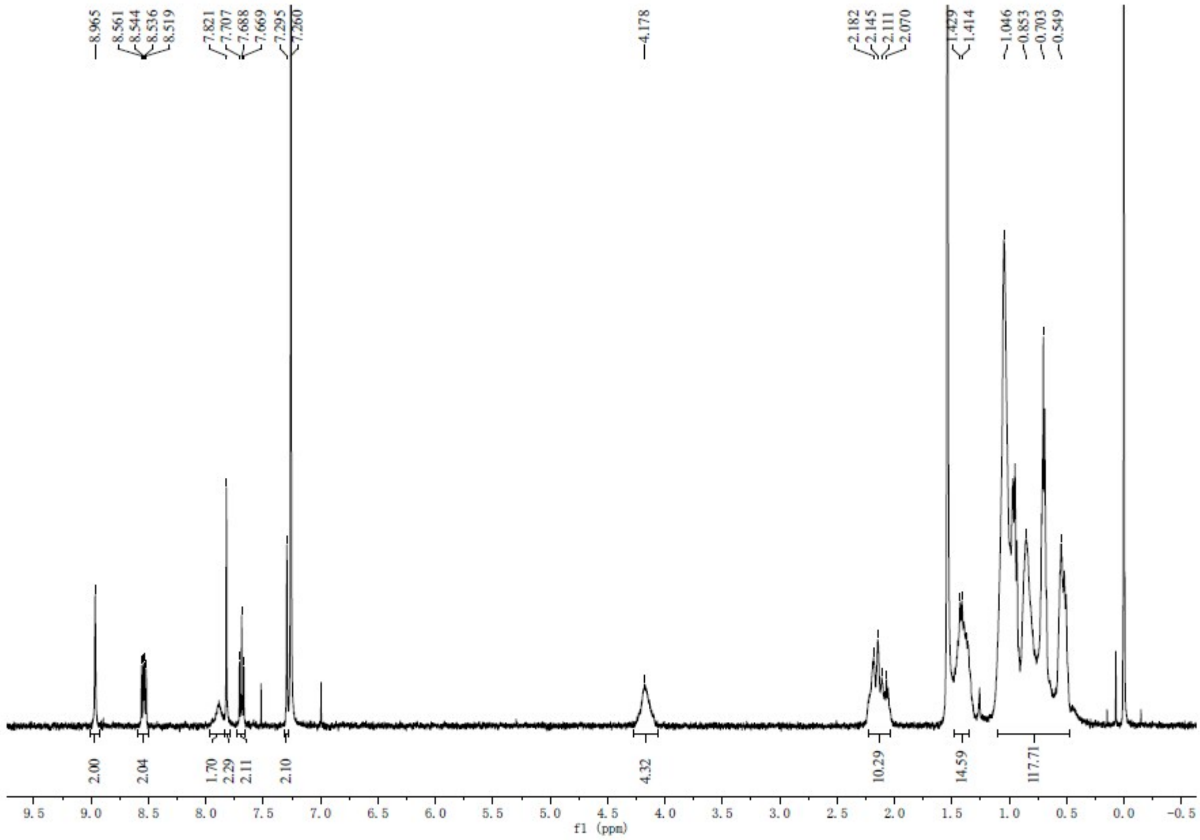
^{1}HNMR

ZITI-N-C_8H_{17}



ZITI-N-EH



High Resolution MALDI-TOF Mass Spectrum of Compound ZITI-N-C_8H_{17}

MALDI,ZJY-2

Analysis Info

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Method	MALDI_P_100-3000	Operator	
Sample Name	MURU-N-ESI	Instrument	solariX
Comment			

Acquisition Parameter

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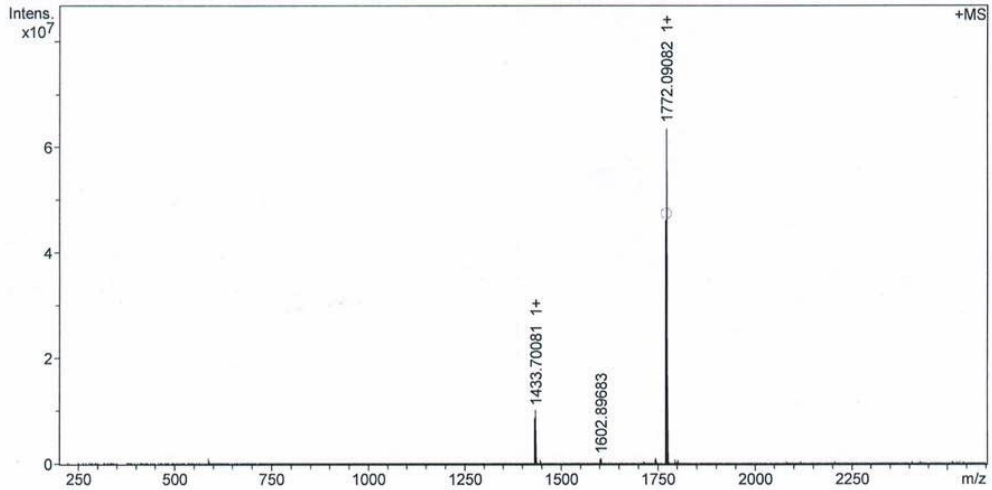
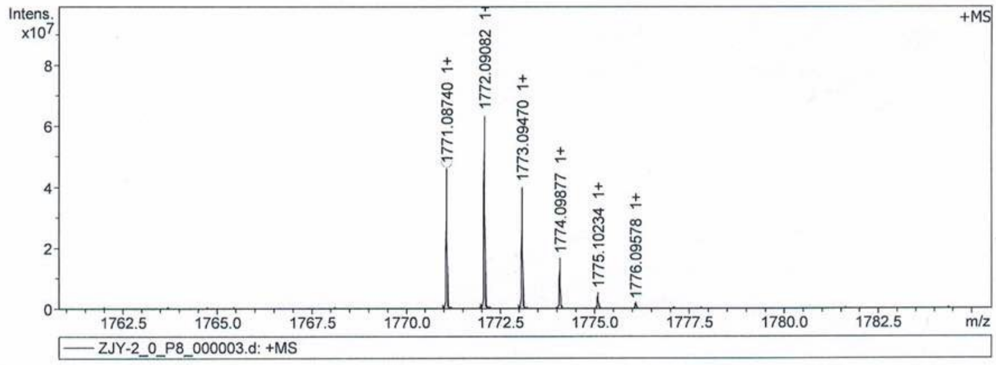
Broadband High Mass	2600.0 m/z	Laser Power	10.2 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				





Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1771.087400	1	C114H146F4N6O2S2	100.00	1771.087934	0.3	-0.3	57.4	43.0	odd	ok

High Resolution MALDI-TOF Mass Spectrum of Compound ZITI-N-EH

ZITI-N(EH)-47

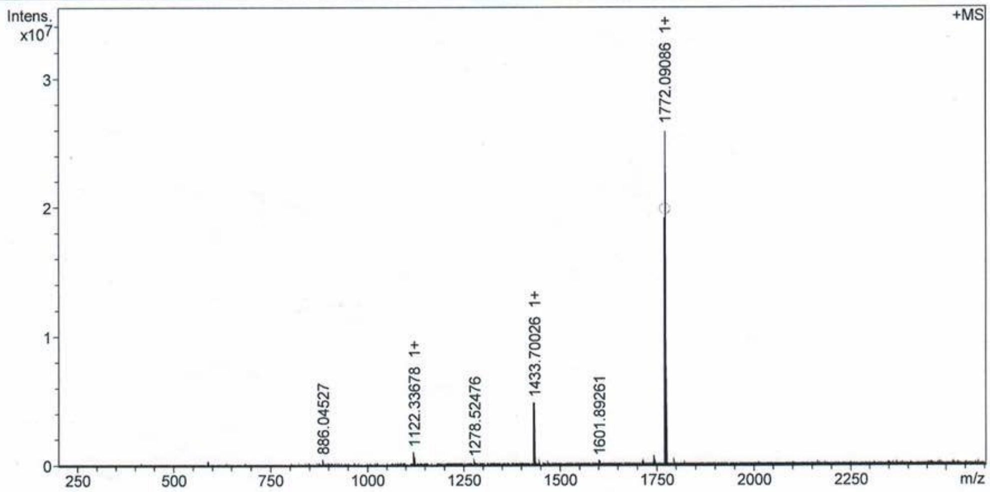
MALDI,3

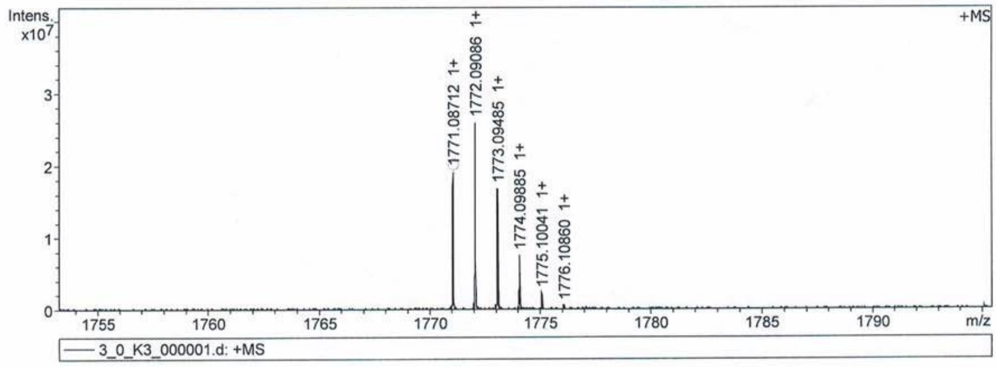
Analysis Info

Analysis Name	D:\Data\MALDI\2019\0725\3_0_K3_000001.d	Acquisition Date	7/25/2019 3:00:49 PM
Method	MALDI_P_100-3000	Operator	
Sample Name	MURU-N-ESI	Instrument	solariX
Comment			

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	2	Calibration Date	Thu Jul 25 02:57:15 2019
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	4194304
Broadband High Mass	2600.0 m/z	Laser Power	10.6 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				





Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1771.087116	1	C114H146F4N6O2S2	100.00	1771.087934	-0.5	-0.4	42.7	43.0	odd	ok