

Synthesis and Photovoltaic Properties of Non-fullerene Acceptor with F-phenylalkoxy as Side Chain

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EXPERIMENTAL SECTION

Measurement instruments

All compounds were characterized by NMR. NMR spectra of the ¹H and ¹³C were recorded on a Bruker AM-400(500) MHz spectrometer in CDCl₃ using tetramethylsilane as an internal reference. The UV-visible absorption spectra were recorded on a UV-2600 spectrophotometer. The cyclic voltammogram of ITIC-FOR was measured by CHI660E electrochemical workstation. The CV analysis was carried out in a 0.1 M solution of tetra-n-butylammonium hexafluorophosphate in anhydrous acetonitrile using a CHI660E electrochemical workstation, a three-electrode cell with platinum electrode as the working electrode, Ag/AgCl as the reference electrode, and a platinum (Pt) wire as the counter electrode. Polymer thin films were coated on the Pt electrode and dried before the experiment. Morphologies were explored by Agilent Technologies, 5500 Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM)(JEM-2100F).¹

Device fabrication

The traditional NF-PSCs with the device structure of indium tin oxide (ITO) / poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS)/active layer/perylene diimide functionalized with amino N-oxide (PDINO)/Al was produced. firstly, ITO was cleaned by cleaning agents, deionized water, then it was ultrasonic washed by acetone and isopropyl. Secondly ITO-coated glass was disposed by UVO for 20min. UVO is ultraviolet-ozone. The aim is to further clean the ITO surface and optimize the function of ITO. Then PEDOT:PSS solution was spin cast on the clean ITO-coated glass substrate, the ITO was annealed at 150 °C for 20 min in an air environment. The active layer of HFQx-T: ITIC-FOR (w/w; 1:1, 1:1.5, 1.5:1) of 20mg/ml in CF solution. the blend solution were spin-coated on PEDOT-PSS film at 3000 rpm in a glovebox to fabricate the active layers. Then the active layers were treated by TA. After that, a cathode buffer layer of PDINO with a concentration of 1mg mL⁻¹ was spin-coated on the surface of active layer with the thickness of 35 nm. Finally, an aluminum electrode (Al, 850 Å) were vacuum-deposited at 6.0 × 10⁻⁵ Pa and the thickness was monitored by a quartz crystal microbalance ².

Synthesis of Compound 1

Dithiophene (4.21 g, 30 mmol) was put in a dry three-necked flask. 150 mL of anhydrous tetrahydrofuran (THF) was added through a constant pressure dropping funnel and stirred at -78°C for 30 min. n-Butyllithium (n-BuLi, 12 mL, 30 mmol) was slowly added and stirred for 60 min. Then, tributyltin chloride (12.63 g, 38.8 mmol) was added in one portion and stirring for 20 min. Subsequently, the solution was warmed to room temperature and stirred overnight. Water was added slowly to the solution and extracted with petroleum ether. The organic phase was collected, and the petroleum ether was removed by rotation, and gave a brown oily liquid as a crude product which was directly subjected to the next reaction.

Synthesis of Compound 2

Compound 1(1.06g,2.46mmol) and diethyl 2,5- dibromoterephthalate (0.43 g, 1.12mmol) were dissolved in dry toluene (10 mL) under Ar for 15 min. Then, Pd(PPh₃)₄ (60 mg, 0.05mmol) was added under Ar. The mixture was refluxing at for 48 h. After completion of the reaction, the reaction mixture was poured into water (100 mL) and extracted with MC. The organic layer was washed by water, and then dried over Na₂SO₄. After solvent removal, the crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and hexane (1:1) as an eluent to afford a yellow solid(0.46 g, yield: 82%) .

¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H), 7.44 (d, *J* = 2.9 Hz, 1H), 7.31 (d, *J* = 4.5 Hz, 1H), 7.30 (s, 1H), 4.30 (s, 2H), 1.21 – 1.09 (m, 3H).¹

Synthesis of Compound 3

n-Buli (2.5M,7.5ml) was added to a mixture of 1 -bromo -3 -fluoro -4 - hexyloxybenzene(4.67g,16.98mmol) in dry tetrahydrofuran (THF, 25ml) ,and then stirred for 30 min at -78°C under Ar, and stirring for 1 h, solution of compound 2 in anhydrous THF (20 mL) was added (1.43 g, 2.88 mmol). Then the mixture was dehydrated in glacial acetic acid (70 mL) and concentrated hydrochloric acid (7 mL) to give a yellow solid(0.87 g, yield:26%).

¹H NMR (400 MHz, CDCl₃) δ 7.44 (s, 2H), 7.33 (s, 4H), 7.04 (d, *J* = 2.2 Hz, 2H), 7.01 (d, *J* = 2.3 Hz, 2H), 6.96 (d, *J* = 1.7 Hz, 2H), 6.94 (d, *J* = 1.7 Hz, 2H), 6.87 (t, *J* = 8.6 Hz, 4H), 3.99 (t, *J* = 6.6 Hz, 8H), 1.80 (m, 8H), 1.39-1.22 (m, 32H), 0.90 (t, *J* = 7.0 Hz, 12H).¹

Synthesis of Compound 4

n-Buli (2.5M,0.9ml) was added to a mixture of compound 3c (0.87 g, 0.75 mmol) in anhydrous THF(30ml), at -78°C under Ar , then stirring for 1 h. anhydrous N,N- dimethylformamide(0.2mL) was added, Stirred overnight at room temperature to give a yellow solid (0.55 g, yield: 61%).

¹H NMR (400 MHz, CDCl₃) δ 10.01 (s, 2H), 8.00 (s, 2H), 7.56 (s, 2H), 7.00-686 (m, 12H), 4.00 (t, *J* = 6.6 Hz, 8H), 1.49-1.25 (m, 32H), 0.88 (t, *J* = 7.0 Hz, 12H).¹

Synthesis of ITIC-FOR

Compound 4 (0.12 g, 0.10mmol) and 3-(dicyanomethylene) fluorenone (0.20 g, 1mmol) were dissolved in a solution of THF(30ml) ,then the mixture was catalyzed by pyridine(1ml) .The mixture was stirred and refluxed overnight. The resulting mixture was extracted with DCM, washed with water, and dried over MgSO₄. After removal the solvent, the crude product was purified on a silica-gel column chromatography to afford 83 mg of compound ITIC-FOR in 53% yield as a dark blue solid .¹H NMR (400 MHz, CDCl₃) δ 8.90 (s, 2H), 8.72 (d, *J* = 7.7 Hz, 2H), 8.25 (s, 2H), 7.95 (d, *J* = 6.8 Hz, 2H), 7.79 (m, 4H), 7.59 (s, 2H), 7.04 (m, 8H), 6.95 (t, *J* = 8.8 Hz, 4H), 4.02 (t, *J* = 6.6 Hz, 8H), 1.81 (m, 8H), 1.44-1.27 (m, 24H), 0.90 (t, *J* = 7.0 Hz, 12H).

^{13}C NMR (126 MHz, CDCl_3) δ 188.09 (s), 160.36 (s), 158.71 (s), 156.03 (s), 152.55 (s), 148.06 (s), 146.86 (s), 143.66 (s), 140.04 (s), 138.18 (s), 137.45 – 136.59 (m), 134.82 (d, $J = 87.7$ Hz), 133.45 (s), 129.07 (s), 125.31 (s), 123.77 (s), 122.80 (s), 118.32 (s), 115.73 – 114.06 (m), 69.44 (s), 68.00 (s), 62.48 (s), 31.79 (s), 28.97 (s), 26.49 (d, $J = 109.0$ Hz), 22.63 (s), 14.07 (s).

HR-MS(MALDI-TOF)m/z calcd. for($\text{C}_{94}\text{H}_{78}\text{F}_4\text{N}_4\text{O}_6\text{S}_4$) :1563.48. Found: 1563.47724

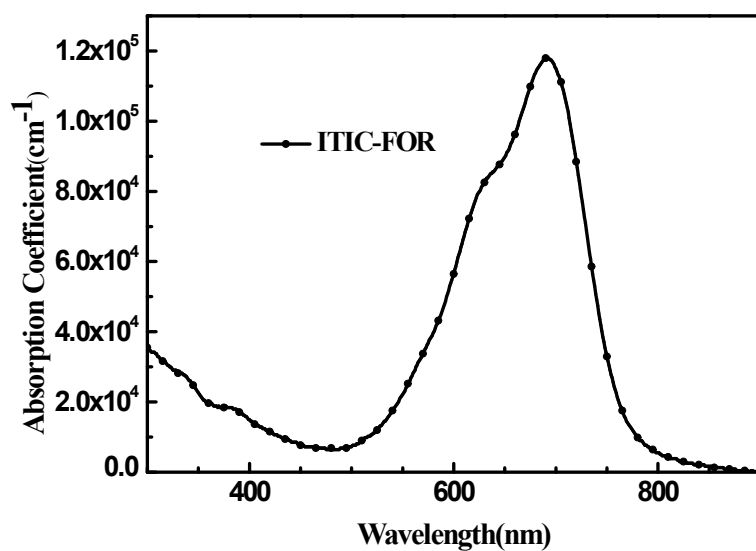


Figure S1 The absorption coefficients spectra of ITIC-FOR(film)

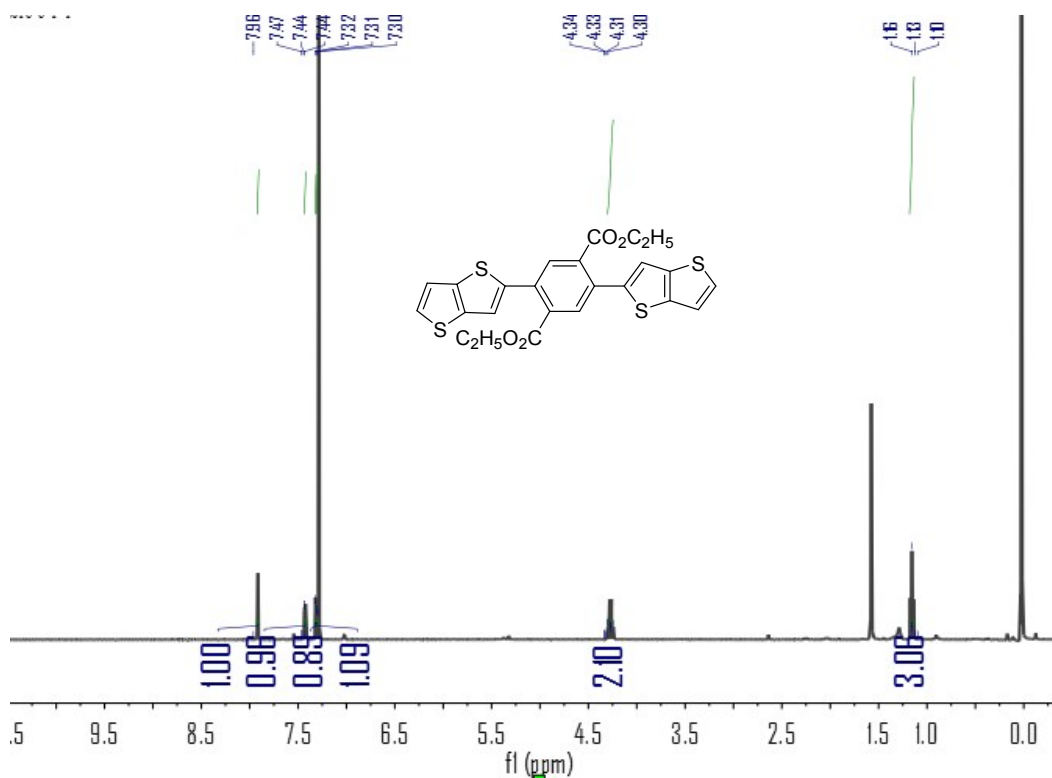
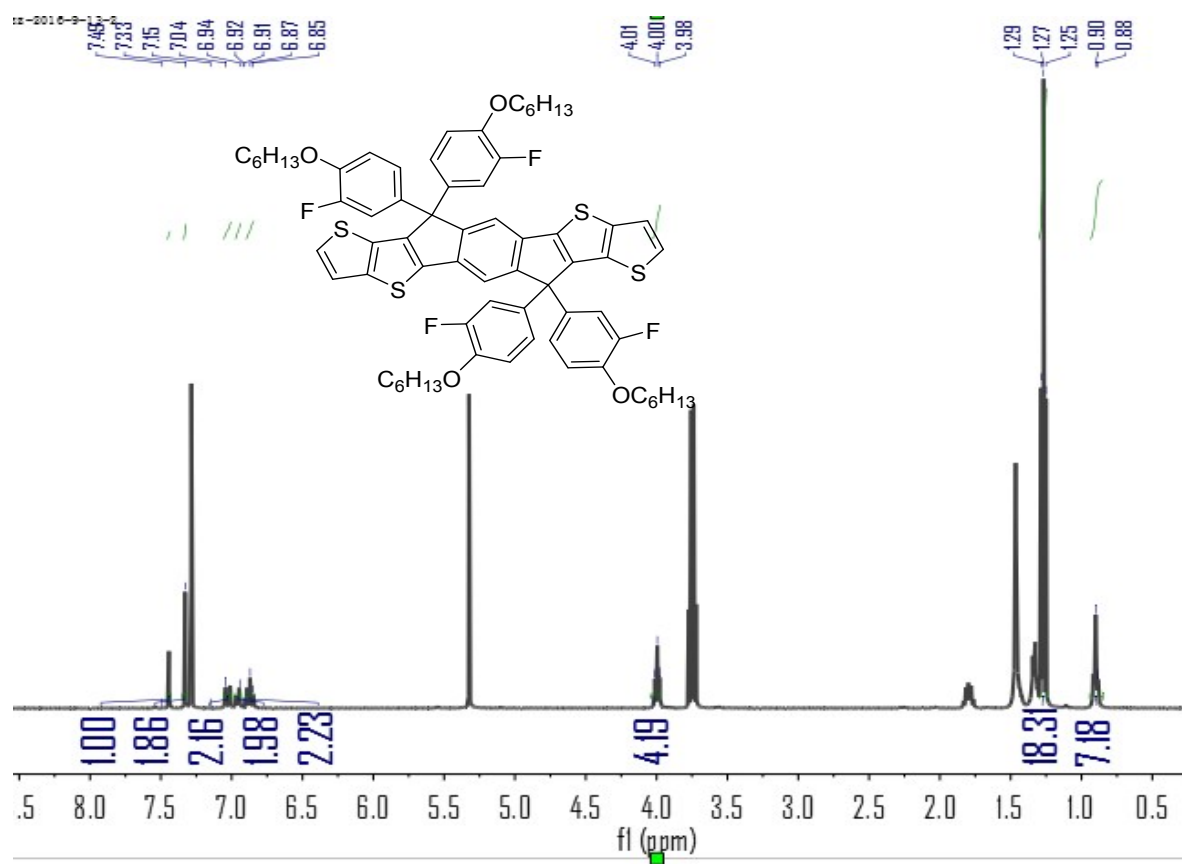


Figure S2 ^1H NMR spectrum of 2



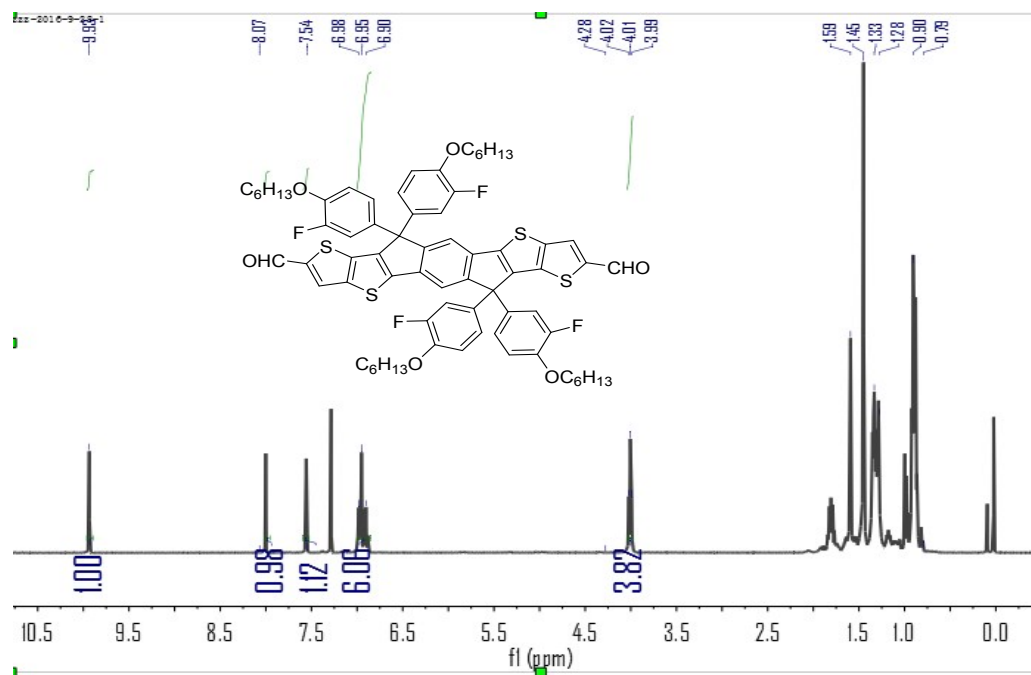
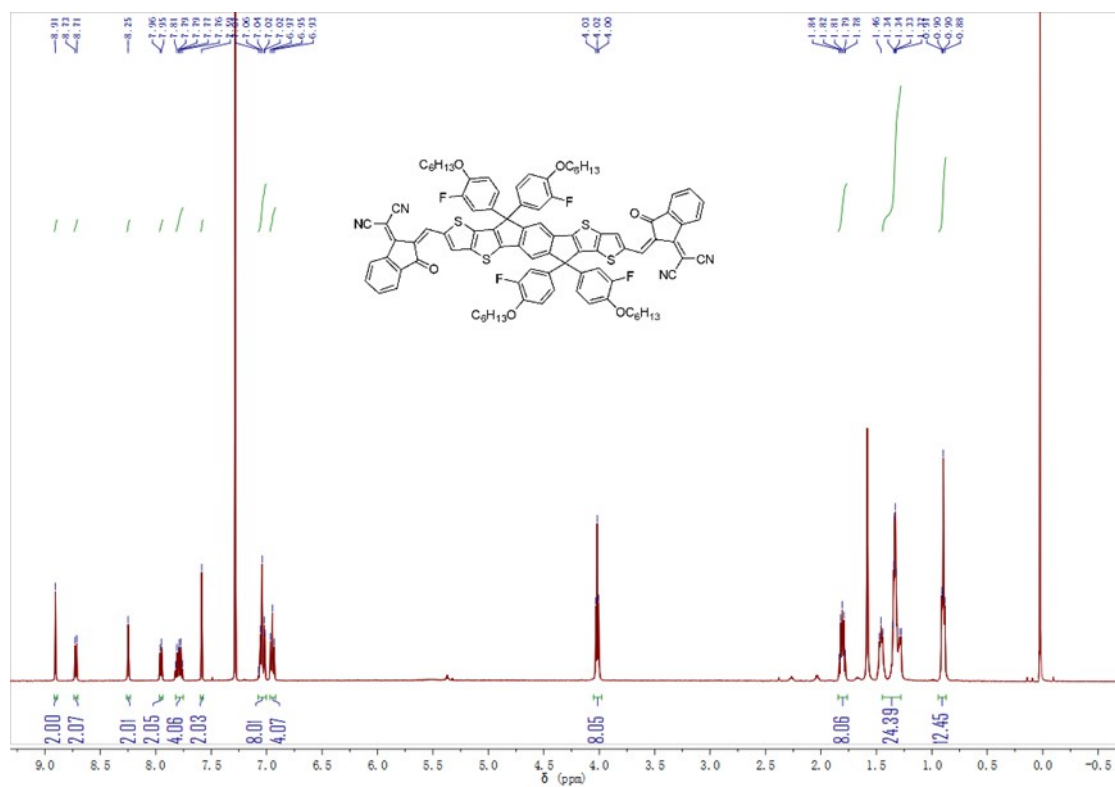


Figure S4 ¹H NMR spectrum of 4



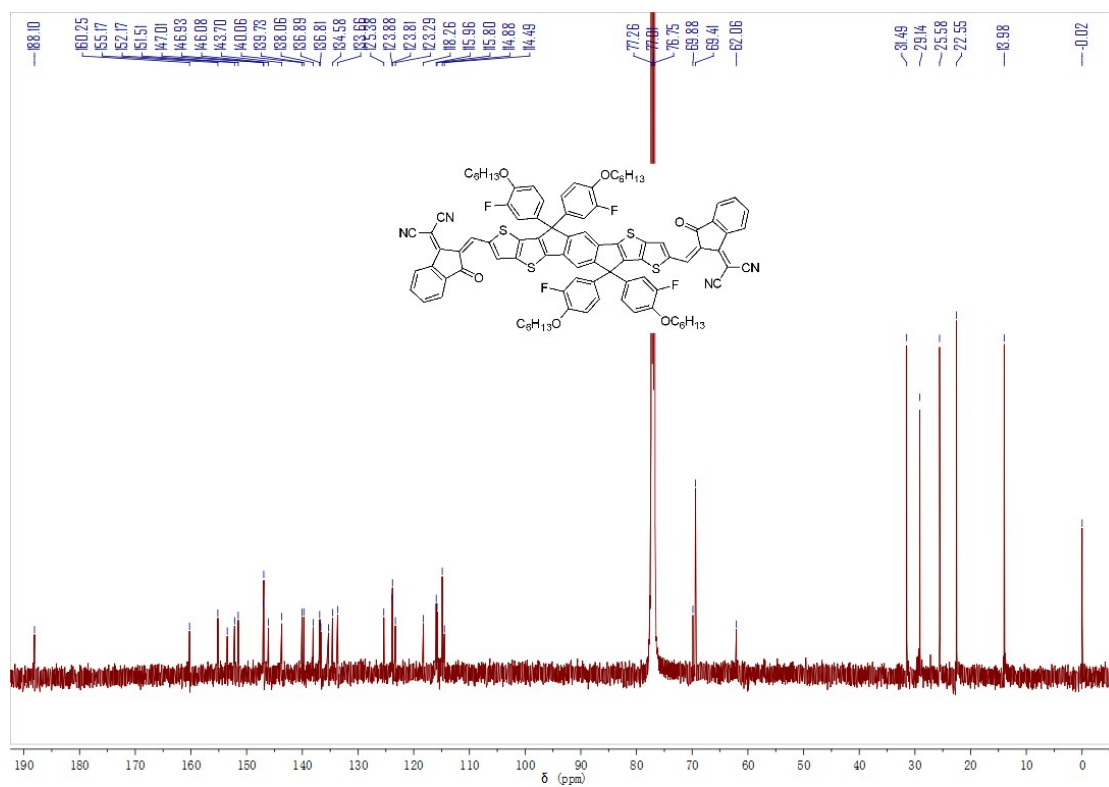


Figure S6 ^{13}C NMR spectrum of ITIC-FOR

ITIC-FOR

MALDI,Z3,20180927

Analysis Info

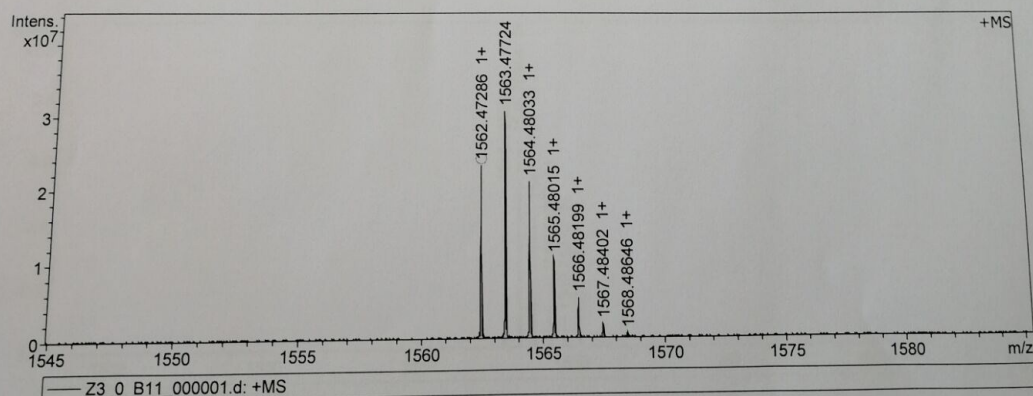
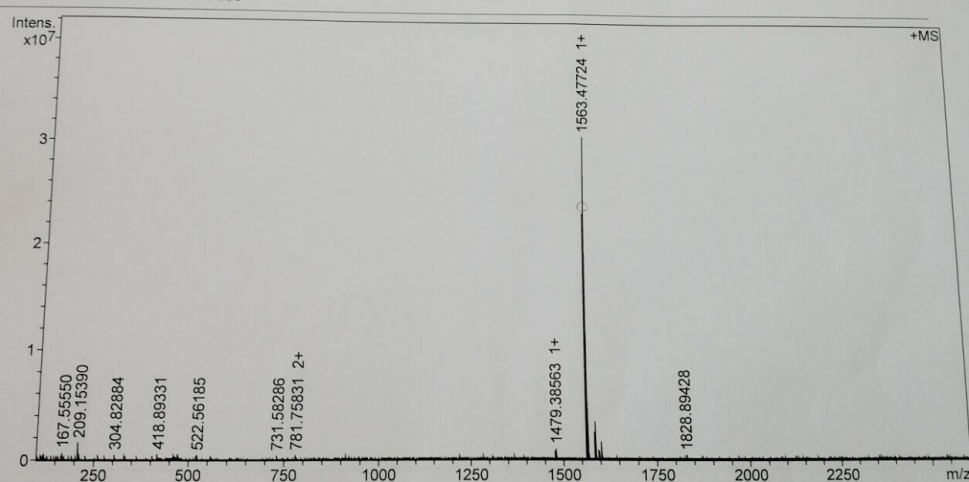
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Method MALDI_P_100-3000
Sample Name MURU-N-ESI
Comment

Acquisition Date 9/27/2018 5:43:10 PM

Operator
Instrument solariX

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	2	Calibration Date	Fri Sep 21 05:09:36 2018
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	101.1 m/z	No. of Laser Shots	10	Data Processing Size	4194304
Broadband High Mass	2600.0 m/z	Laser Power	28.6 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
1562.472858	1	C94H78F4N4O6S4	100.00	1562.473485	0.4	-0.8	62.6	56.0	odd	ok

Figure S7 The high resolution mass spectrum (MALDI-TOF) of ITIC-FOR

References

1. Z. Zhang, L. Feng, S. Xu, Y. Liu, H. Peng, Z. G. Zhang, Y. Li and Y. Zou, *Adv Sci (Weinh)*, 2017, **4**, 1700152.
2. W. Zhao, S. Zhang and J. Hou, *Science China Chemistry*, 2016, **59**, 1574-1582.