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Electronic Supporting Information for

Enhancing performance of non-fullerene organic solar cells via end group engineering of fused-ring electron acceptors†

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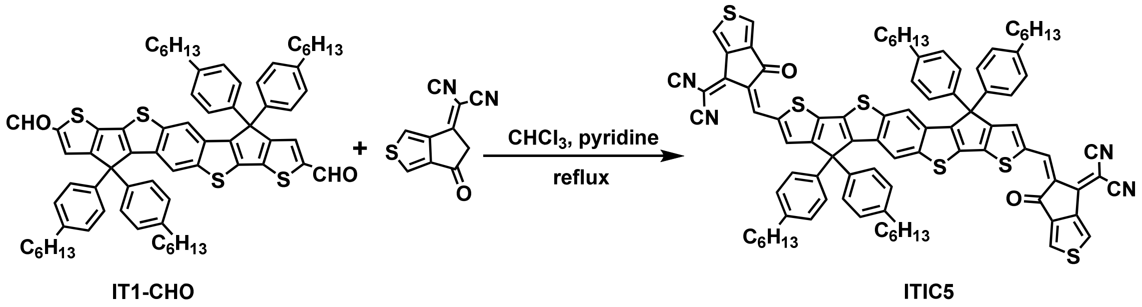
Materials synthesis

Unless stated otherwise, all the solvents and chemical reagents were obtained commercially and used without further purification. **Scheme S1** shows the synthetic route for ITIC5. Compound ITIC1 was synthesized according to our previously published procedures[S1]. J71 was purchased from Solarmer Inc.



Scheme S1 Synthetic route for ITIC5.

To a solution of compound IT1-CHO (60 mg, 0.06 mmol) and 2-(6-oxo-5,6-dihydro-4H-cyclopenta[c]thiophen-4-ylidene)malononitrile (50 mg, 0.25 mmol) in dry $CHCl_3$ (20 mL) was added pyridine (0.3 mL) under argon. The mixture was refluxed for 16 h and then allowed to cool to room temperature, then the mixture was poured into CH_3OH (100 mL) and filtered, the residue left in filter paper was dissolved by $CHCl_3$. After removing the solvent, the residue was purified using column chromatography on silica gel employing petroleum ether/CH_2Cl_2 (1:1, v/v) as an eluent, yielding a dark blue solid (52 mg, 64%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.75 (s, 2H), 8.25 (d, J = 2.1 Hz, 2H), 8.03 (s, 2H), 7.81 (d, J = 2.4 Hz, 2H), 7.65 (s, 2H), 7.14 (m, 16H), 2.56 (t, J = 7.2 Hz, 8H), 1.59 (m, 8H), 1.33 (m, 24H), 0.87 (t, $J = 6.6$ Hz, 12H). ^{13}C-NMR (75 MHz, $CDCl_3$): 181.67, 163.00, 156.31, 156.19, 156.11, 144.16, 142.81, 142.56, 142.23, 140.68, 139.42, 139.00, 138.24, 137.33, 131.85, 129.06, 128.12, 127.90, 127.67, 125.51, 118.33, 115.23, 114.59, 67.11, 62.85, 35.68, 31.80, 31.38, 29.22, 22.70, 14.22. HR-MS (MALDI-TOF): Calc. for $C_{90}H_{78}N_4O_2S_6$: 1439.4483. Found: 1439.43496. Anal. Calc. for $C_{90}H_{78}N_4O_2S_6$: C, 75.07; H, 5.46; N, 3.89. Found: C, 75.10; H, 5. 18; N, 3.79.

Characterization

The ^{1}H NMR and ^{13}C NMR spectra were measured on Bruker AVANCE 300 MHz spectrometer. Mass spectra were measured on an AB Sciex MALDI-TOF/TOF Mass Spectrometer using MALDI mode. Elemental analyses were carried out using an Elementar Analysensysteme GmbH vario EL Elemental Analyzer. Solution (chloroform) and thin film (on quartz substrate) UV-vis absorption spectra were recorded on a JΛSCO V-570 spectrophotometer. Electrochemical measurements were carried out under nitrogen on a deoxygenated solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M) in CH_3CN using a computer-controlled CHI660C electrochemical workstation, a glassy-carbon working electrode coated with samples, a platinum-wire auxiliary electrode, and an Ag/AgCl as a reference electrode. Potentials were referenced to ferrocenium/ferrocene ($FeCp_2^{+/0}$) couple by using ferrocene as an internal standard. Thermogravimetric analysis (TGA) measurements were performed on a TA Q600 TGA-DSC-DTA (Q600 SDT) under a nitrogen flow at a heating rate of

10 °C min^{-1}. The thickness of active layer was measured on a Bruker DektakXT profilometer.

AFM measurements were performed on a Multimode 8 atomic force microscope (Bruker) in tapping mode. TEM measurements were performed on a JEM-2100 transmission electron microscope operated at 200 kV. The samples for the TEM measurements were prepared as follows: the active-layer films were spin-cast onto ITO/PEDOT:PSS substrates, and the substrates with the active layers were submerged in deionized water to make the active layers float on the air-water interface. Then, the floated films were picked up on unsupported 200 mesh copper grids for the TEM measurements. The grazing incidence X-ray scattering measurements (GIWAXS and GISAXS) were carried out at BL14B1 and BL19U2, respectively, of Shanghai Synchrotron Radiation Facility, Shanghai. For GIWAXS, the energy of the X-ray source was set to 10 keV (wavelength of 1.24 Å) and the incident angle was 0.15°. For GISAXS, the energy of the X-ray source was set to 12 keV (wavelength of 1.03 Å) and the incident angle was 0.10°.

Fabrication and characterization of organic solar cells

Organic solar cells were fabricated with the structure: ITO/PEDOT:PSS/active layer/ Zracac/Al. The patterned ITO glass (sheet resistance = 10 $\Omega\ \square^{-1}$) was first cleaned with detergent, ultrasonicated in deionized water, acetone and isopropanol, dried in an oven and then treated in ultraviolet-ozone chamber (Jelight Company, USA) for 30 min. A thin layer (35 nm) of PEDOT:PSS (Baytron PVP AI 4083, Germany) was spin-coated onto the ITO glass and baked at 150 °C for 20 min. A chloroform solution of J71:acceptor (14 mg mL^{-1} in total) was spin-coated on PEDOT:PSS layer to form a photoactive layer (*ca.* 100 nm). A thin layer of Zracac in ethanol with a concentration of 1.4 mg mL^{-1} was spin-coated atop the active layer at a spin coating rate of 3500 rpm. Finally, an aluminum (Al) layer (*ca.* 90 nm) was evaporated onto the surface at the vacuum condition of *ca.* 10^{-5} Pa. The active area of the devices was 4 mm^2. The *J-V* curve was measured using a computer-controlled B2912A Precision Source/Measure Unit (Agilent Technologies). An XES-70S1 (SAN-EI Electric Co., Ltd.) solar simulator (AAA grade, 70 × 70 mm^2 photobeam size) coupled with AM 1.5G solar spectrum filters was used as the light source, and the optical power at the sample was 100 mW cm^{-2}. A 2×2 cm^2 monocrystalline silicon reference cell (SRC-1000-TC-QZ) was purchased from VLSI Standards Inc. The EQE spectra were measured using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.). The light intensity at each wavelength was calibrated using a standard single crystal Si photovoltaic cell.

Mobility measurements

Hole-only and electron-only diodes were fabricated using the architectures of ITO/PEDOT:PSS/active layer/Au and Al/active layer/Al, respectively. Mobilities were extracted by fitting the current density–voltage curves using SCLC method. The *J-V* curves of the devices were plotted as $\ln(Jd^3V^{-2})$ versus $(V/d)^{0.5}$ using the equation $\ln(Jd^3V^{-2}) \cong 0.89(1/E_0)^{0.5}(V/d)^{0.5} + \ln(9\varepsilon_0\varepsilon_r\mu/8)$, where J is the current density, d is the film thickness of active layer, μ is the hole or electron mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), $V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage to the device, and V_{bi} is the built-in voltage due to the difference in work functions of the two electrodes (for hole-only diodes, V_{bi} is 0.2 V; for electron-only diodes, V_{bi} is 0 V).

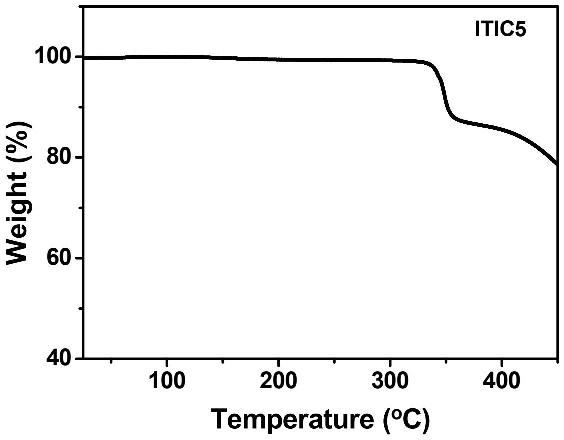


Fig. S1 TGA curve of ITIC5.

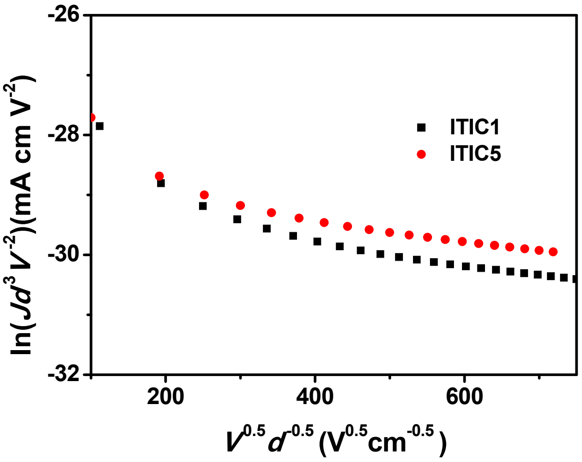


Fig. S2 *J-V* characteristics in dark for electron-only devices based on ITIC1 and ITIC5.

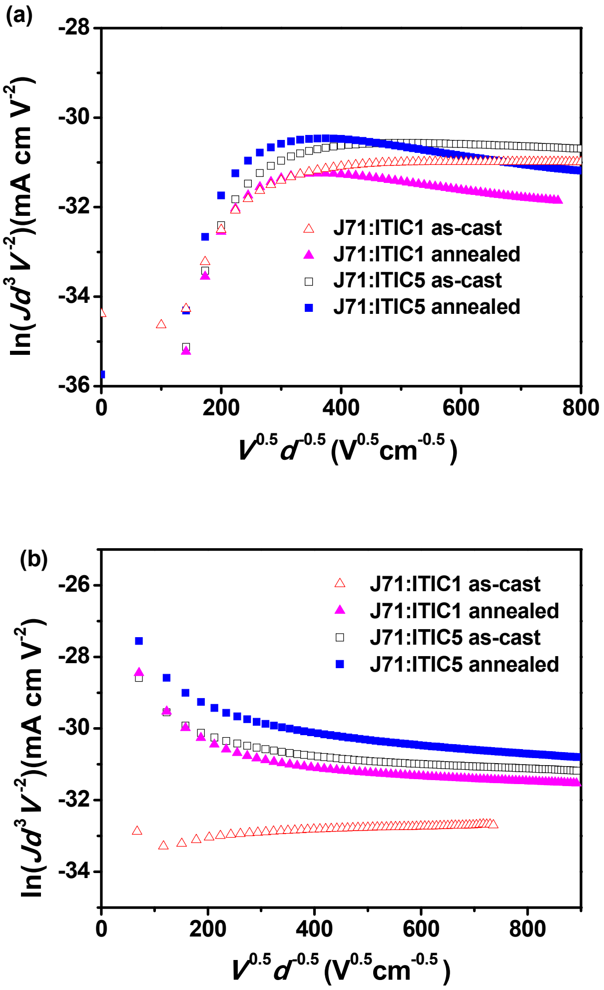


Fig. S3 *J*-*V* characteristics in dark for (a) hole-only and (b) electron-only devices based on J71:ITIC1 and J71:ITIC5 blends.

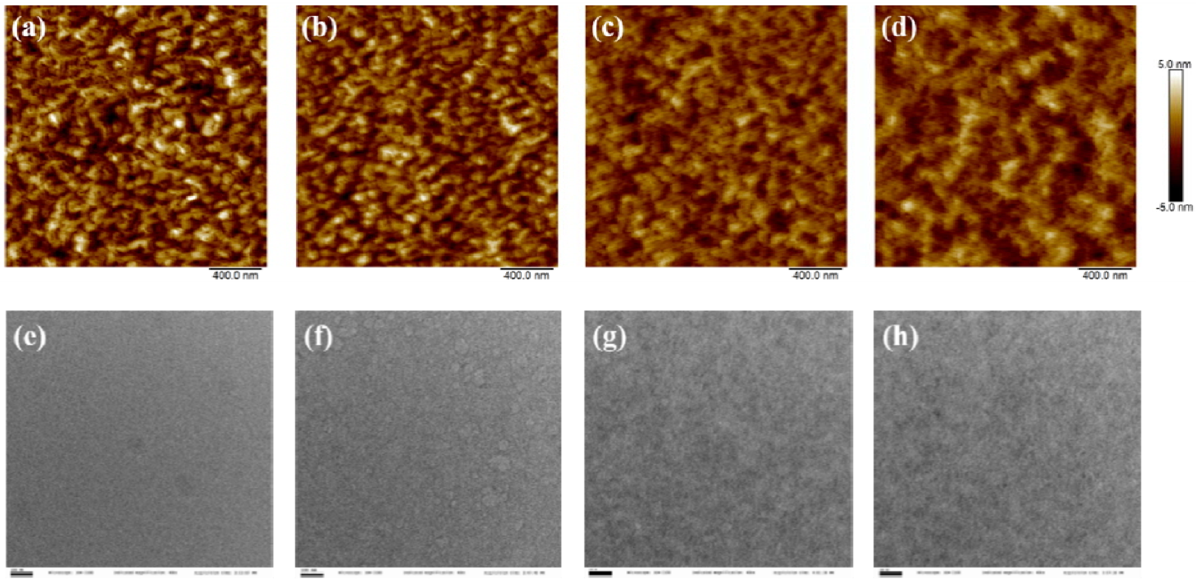


Fig. S4 AFM height images (a-d scale bar: 400 nm) and TEM images (e-h scale bar: 100 nm): (a,e) J71:ITIC1 as-cast, (b,f) J71:ITIC1 annealed, (c,g) J71:ITIC5 as-cast and (d,h) J71:ITIC5 annealed films.

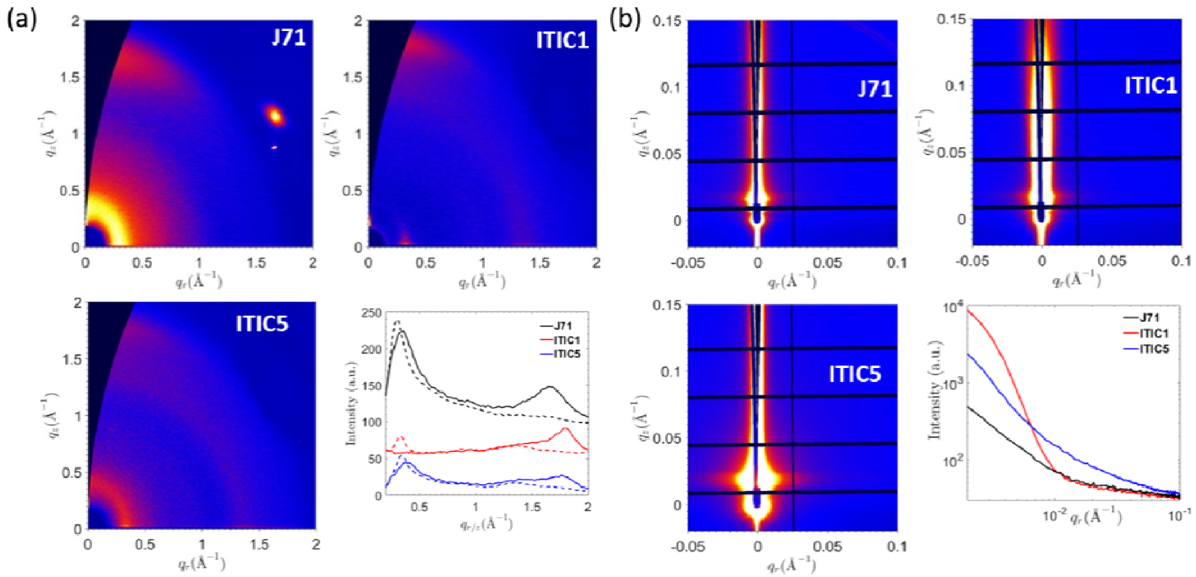


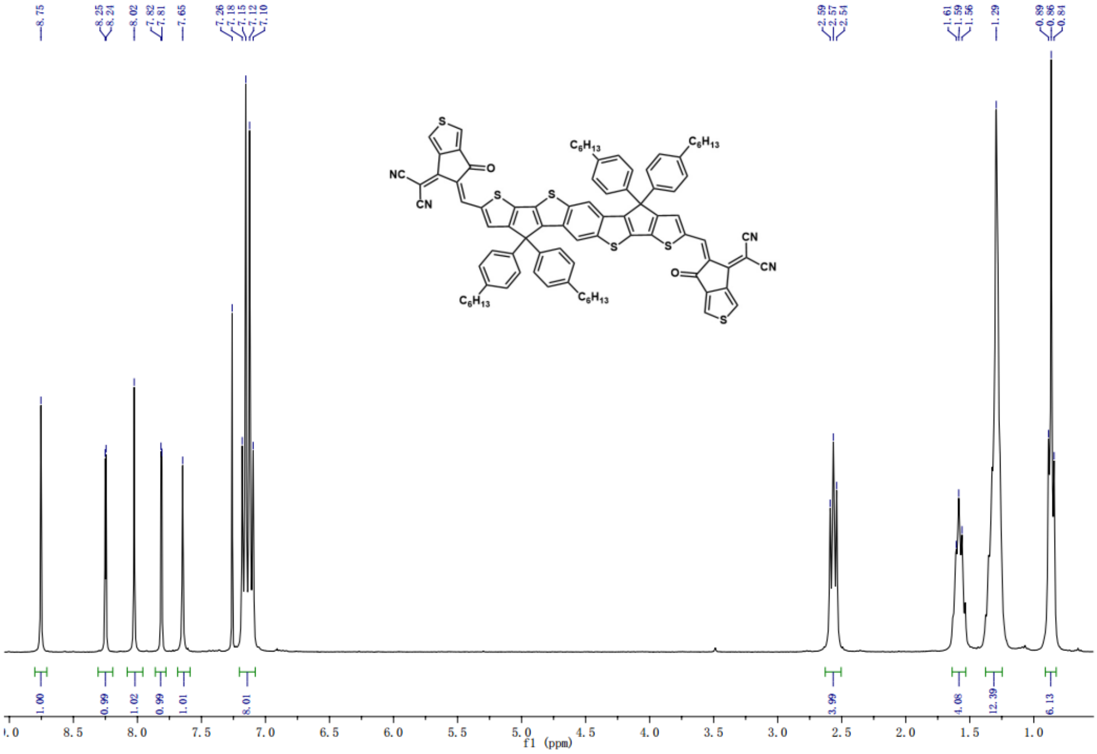
Fig. S5 (a) 2D GIWAXS patterns of pure J71, ITIC1 and ITIC5 films and the corresponding GIWAXS intensity profiles along the in-plane (dashed line) and out-of-plane (solid line) directions. (b) The GISAXS patterns and the corresponding intensity profiles along the in-plane direction.

Table S1 The optimization of the devices.

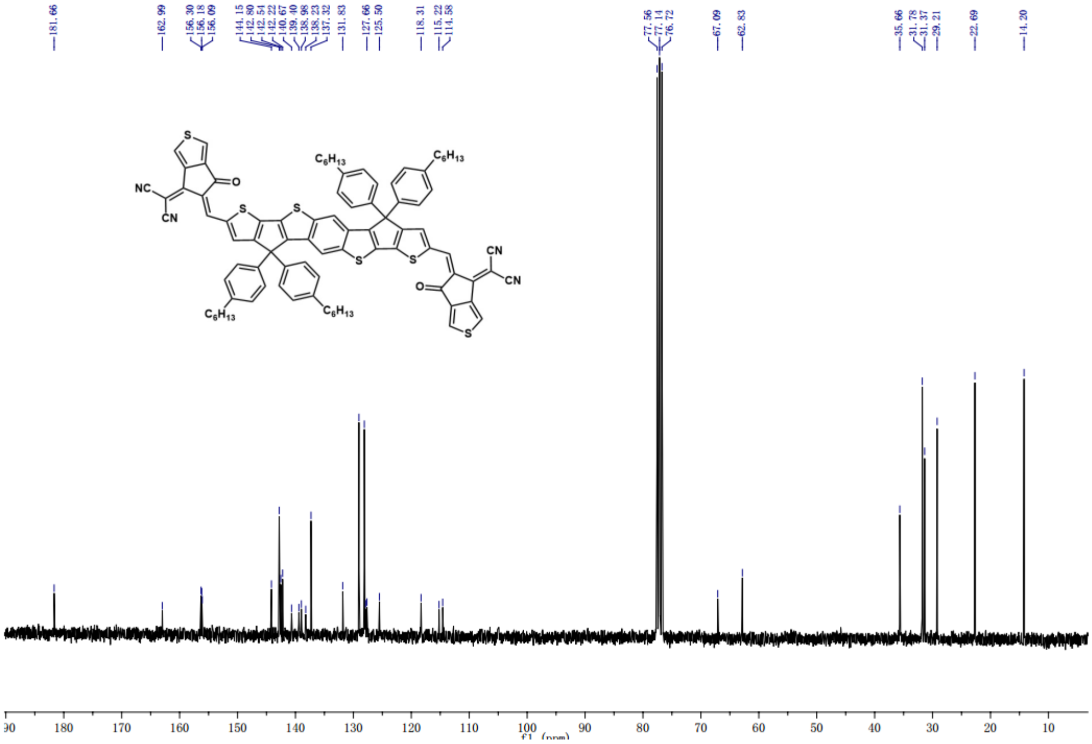
device	D:A (w/w)	Thermal annealing	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
J71:ITIC1	1.5:1	100 ℃ 5 min	0.920±0.002 (0.921)	15.21±0.14 (15.56)	58.1±1.0 (59.2)	8.14±0.3 (8.48)
	1:1	-	0.904±0.003 (0.904)	15.01±0.49 (16.08)	57.4±1.3 (57.9)	7.80±0.3 (8.41)
	1:1	100 ℃ 5 min	0.920±0.003 (0.921)	14.94±0.48 (15.74)	61.2±1.6 (62.0)	8.47±0.3 (8.99)
	1:1.5	100 ℃ 5 min	0.903±0.003 (0.905)	14.50±0.19 (14.71)	54.3±1.1 (55.5)	7.11±0.2 (7.39)
J71:ITIC5	1.5:1	100 ℃ 5 min	0.904±0.003 (0.908)	17.01±0.12 (17.07)	67.6±0.8 (68.3)	10.4±0.1 (10.6)
	1:1	-	0.898±0.003 (0.900)	17.35±0.19 (17.47)	69.7±0.6 (70.0)	10.8±0.1 (11.0)
	1:1	100 ℃ 5 min	0.892±0.003 (0.897)	18.35±0.13 (18.48)	74.7±0.6 (75.5)	12.2±0.2 (12.5)
	1:1.5	100 ℃ 5 min	0.877±0.004 (0.874)	17.98±0.10 (18.11)	71.2±0.4 (71.6)	11.2±0.1 (11.3)

The values in parentheses are the parameters of the best device.

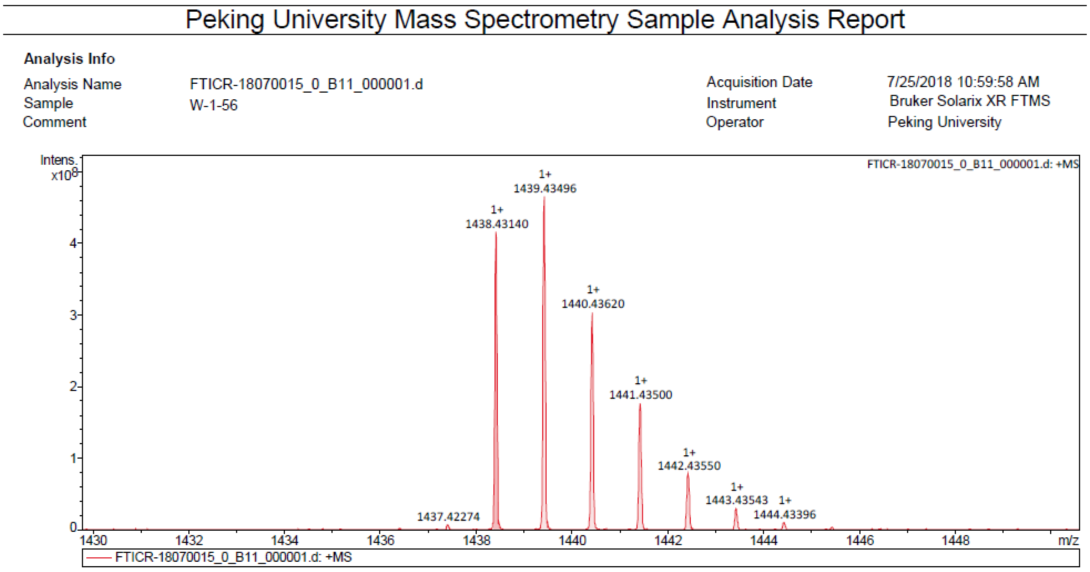
^{1}H NMR spectrum of ITIC5



^{13}C NMR spectrum of ITIC5



HR-MS of ITIC5


Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

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Sample W-1-56
Comment

Acquisition Date 7/25/2018 10:59:58 AM
Instrument Bruker Solarix XR FTMS
Operator Peking University

References

S1. J. Wang, W. Wang, X. Wang, Y. Wu, Q. Zhang, C. Yan, W. Ma, W. You and X. Zhan, *Adv. Mater.*, 2017, **29**, 1702125.