Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Improving the Performance of Organic Solar Cells by Side Chain Engineering of Fused Ring Electron Acceptors

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1.1 Material and Instruments.

Unless otherwise noted, all chemicals were purchased from Aldrich or Acros and used without further purification. Unless otherwise noted, all reactions were performed under an atmosphere of nitrogen and monitored by thin layer chromatography (TLC) on silica gel. Column chromatography was carried out on silica gel (200-300 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400/500 spectrometer. UV-visible absorption spectra were obtained on a PerkinElmer UV-vis spectrometer model Lambda 750. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode. The thickness of the blend films was determined by a Dektak 6 M surface profilometer. The electrochemical behavior of the polymers was investigated using cyclic voltammetry with a standard three-electrode electrochemical cell in a 0.1 M Bu_4NPF_6 solution in CH_3CN at room temperature under an atmosphere of nitrogen with a scanning rate of 0.1 V/S. A Pt plate working electrode, a Pt wire counter electrode, and an $Ag/AgNO_3$ (0.01 M in CH_3CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (F_c) redox system and assumption that the energy level of F_c is 4.8 eV below vacuum. The GIWAXS measurements were conducted on a Xenocs-SAXS/WAXS system with X-ray wavelength of 1.5418 Å. Pilatus 300 K was used as a 2D detector. In addition, the gaps of the detector were erased with a virtual detector function.

1.2 Solar Cells Fabrication and Characterization

PSCs were fabricated with the device configuration of ITO/ZnO/active layer (100 nm)/MoO_3 (85 Å)/Ag (100 nm). The conductivity of ITO is 20 Ω. A mixture of PM6 and acceptor molecule (**4TIC-2F**, **4TIC-C8-2F** and **4TIC-OC8-2F**) in 1,2-dichlorobenzene (DCB) was stirred at 110 ^{o}C at least two hours to ensure sufficient dissolution and then the blend solution was spin-coated onto ZnO layer to form active layer. On one substrate five cells with an effective area of 0.04 cm^2 for each were fabricated. Current-voltage characteristics were recorded using an Enli Technology

Ltd., Taiwan (SS-F53A) under an AM 1.5G AAA class solar simulator with an intensity of 100 mW cm^{-2} as the white light source and the intensity was calibrated with a standard single crystal Si photovoltaic cell. The temperature while measuring the *J-V* curves was approximately 25 °C. The EQE measurements of PSCs were performed by the solar cell spectral response measurement system QE-R3011 (Enli Technology Ltd., Taiwan), which was calibrated by monocrystalline silicon solar cell in advance.

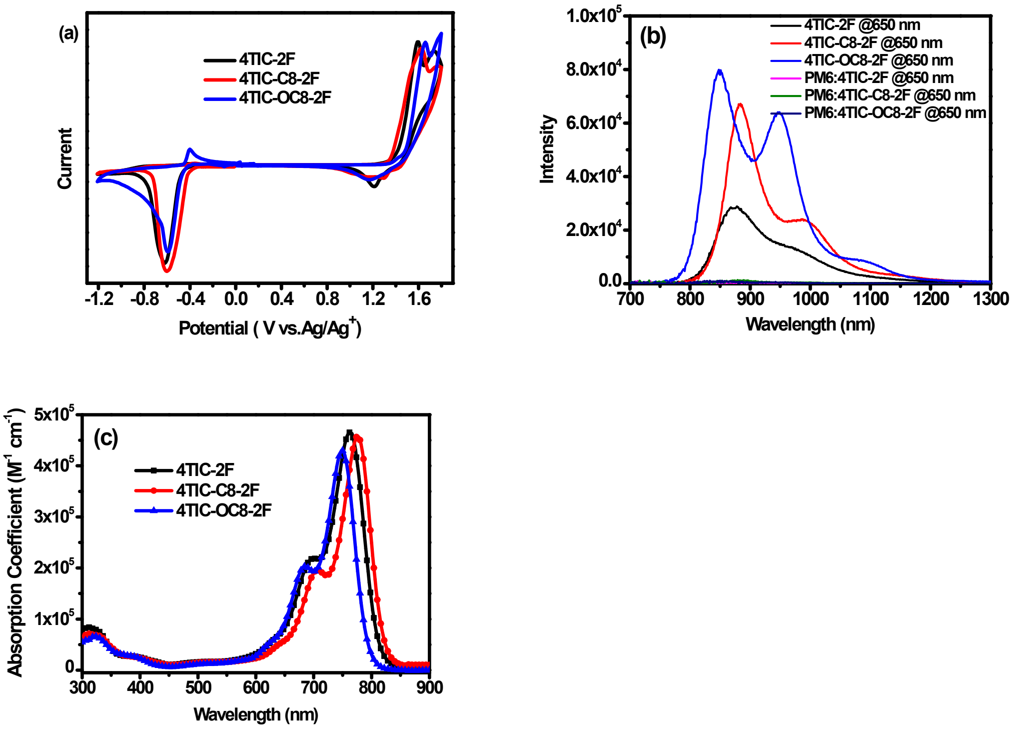


Figure S1. (a) CV curves of **4TIC-2F**, **4TIC-C8-2F** and **4TIC-OC8-2F**, (b) PL intensity of neat and blend films based on **4TIC-2F**, **4TIC-C8-2F** and **4TIC-OC8-2F**, (c) UV-absorption coefficiency of **4TIC-2F**, **4TIC-C8-2F** and **4TIC-OC8-2F** in dilute chloroform solutions.

Table S1. Photovoltaic performance of devices fabricated with **PM6**:**4TIC-2F**.

D:A	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE
1:0.75	0.80	18.62	62.76	9.36

1:1	0.79	18.90	66.8	10.03
1:1.25	0.79	19.05	64.98	9.78

Table S2. Photovoltaic performance of devices fabricated with **PM6**:**4TIC-2F**.

D:A	Additives	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE
1:1	---	0.79	18.90	66.8	10.03
	0.2% 1-CN	0.79	19.28	65.9	9.98
	0.5% 1-CN	0.79	19.44	63.9	9.88
	0.7% 1-CN	0.79	18.94	64.0	9.52

Table S3. Photovoltaic performance of devices fabricated with **PM6**:**4TIC-C8-2F**.

D:A	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE
1:0.75	0.82	19.48	62.7	10.02
1:1	0.83	20.02	64.5	10.75
1:1.25	0.82	19.85	62.4	10.14

Table S4. Photovoltaic performance of devices fabricated with **PM6**:**4TIC-C8-2F**.

D:A	Additives	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE
1:1	---	0.83	20.02	64.5	10.75
	0.7% 1-CN	0.83	20.27	64.4	10.78
	1% 1-CN	0.83	21.41	64.8	11.46
	1.3% 1-CN	0.84	19.43	64.74	10.55

Table S5. Photovoltaic performance of devices fabricated with **PM6**:**4TIC-C8-2F** at 1% 1-CN.

Annealing Temperature	Annealing Time	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE
---	---	0.83	21.41	64.8	11.46
120 °C	5 min	0.79	21.86	67.6	11.68
140 °C	3 min	0.79	22.32	68.08	11.98
	5 min	0.78	22.70	71.5	12.65

	10 min	0.79	21.17	69.0	11.52
160 °C	5 min	0.78	21.69	69.3	11.74

Table S6. Photovoltaic performance of devices fabricated with **PM6:4TIC-OC8-2F**.

D:A	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE
1:0.75	0.85	17.89	64.30	9.75
1:1	0.85	18.82	63.70	10.13
1:1.25	0.84	18.51	64.29	10.00

Table S7. Photovoltaic performance of devices fabricated with **PM6:4TIC-OC8-2F**.

D:A	Additives	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE
1:1	---	0.85	18.82	63.70	10.13
	0.5% 1-CN	0.81	18.42	66.22	9.88
	0.7% 1-CN	0.82	17.98	65.91	9.79
	1.0% 1-CN	0.82	18.34	63.58	9.56

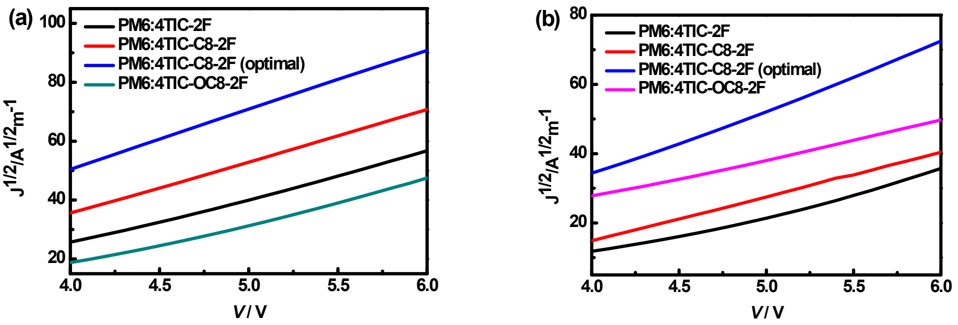


Figure S2. $J^{1/2}$-V curves of hole-only (a) and electron-only (b) devices based on **4TIC-2F**, **4TIC-C8-2F** and **4TIC-OC8-2F**.

Table S8. Hole and electron mobilities of devices based on 4TIC-2F, 4TIC-C8-2F and 4TIC-OC8-2F.

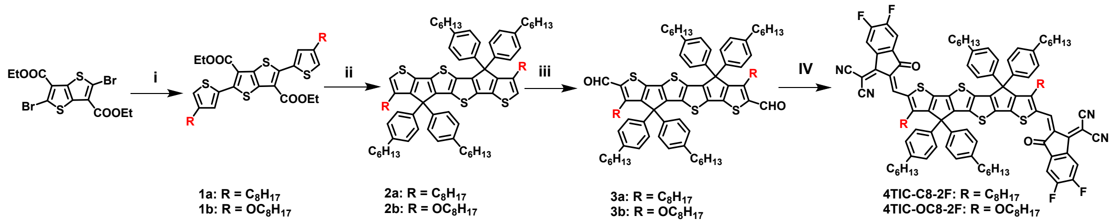
	μ_h (cm^{2}V^{-1}s^{-1})	μ_e (cm^{2}V^{-1}s^{-1})	μ_h/μ_e
PM6:4TIC-2F	8.06×10^{-5}	4.76×10^{-5}	1.69
PM6:4TIC-C8-2F	1.04×10^{-4}	6.82×10^{-5}	1.52

PM6:4TIC-C8-2F[a]	1.37×10^{-4}	1.22×10^{-4}	1.12
PM6:4TIC-OC8-2F	6.97×10^{-5}	4.10×10^{-5}	1.70

[a] 1% 1-CN and 140 °C for 5 min;

Table S9. GIWAXS data of neat acceptors in (010) diffraction peaks.

Acceptor	FWHM ($Å^{-1}$)	CCL (nm)	π-π stacking ($Å^{-1}$)	π-π stacking distance (Å)
4TIC-2F	0.604	10.4	1.49	4.21
4TIC-C8-2F	0.678	9.3	1.45	4.33
4TIC-OC8-2F	0.224	28.1	1.70	3.69



The starting materials diethyl 2,5-dibromothieno[3,2-b]thiophene-3,6-dicarboxylate, tributyl(4-octylthiophen-2-yl)stannane, and tributyl(4-(octyloxy)thiophen-2-yl)stannane were synthesized according to previous reported literatures.

Compound 1a:

A mixture of 2,5-dibromothieno[3,2-b]thiophene-3,6-dicarboxylate (1g, 2.26 mmol), tributyl(4-octylthiophen-2-yl)stannane (3.29 g, 6.78 mmol), and toluene (30 mL) was carefully degassed before and after $Pd(PPh_3)_4$ (78 mg, 0.07 mmol) was added. The mixture was stirred and refluxed overnight. After the reaction finished, the organic solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel eluting with petrol ether/DCM (2:1) to give compound 1a as a light yellow solid (1.21 g, 81%). ^1H NMR (500MHz, $CDCl_3$) δ: 7.39 (d, *J* = 1.15 Hz, 2H), 7.05 (d, *J* = 1.15 Hz, 2H), 4.37-4.40 (m, 4H), 2.62 (t, *J* = 6.35 Hz, 4H), 1.62-1.67 (m, 4H), 1.40 (t, *J* = 5.95 Hz, 6H), 1.26-1.36 (m, 20H), 0.88 (t, *J* = 5.70 Hz, 6H).

^{13}C NMR (125MHz, CDCl$_3$) δ: 161.92, 146.67, 143.61, 137.02, 133.58, 131.20, 123.41, 119.30, 61.29, 31.90, 30.47, 29.44, 29.36, 29.28, 22.69, 14.29, 14.13.

Compound 1b:

Compound 1b was synthesized according to the similar procedure of compound 1a (1.50 g, 85%). ^{1}H NMR (400MHz, CDCl$_3$) δ: 7.29 (d, *J* = 1.4 Hz, 2H), 6.41 (d, *J* = 1.4 Hz, 2H), 4.43 (q, *J* = 6.5 Hz, 4H), 3.90 (d, *J* = 5.6 Hz, 4H), 1.70-1.76 (m, 4H), 1.41-1.20(m, 26H), 0.96-0.90 (m, 6H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ: 162.77, 158.80,146.57, 138.23, 132.55, 123.84, 118.89, 100.88, 70.59, 61.36,40.39, 31.55, 29.08, 23.59, 22.82, 15.19, 13.06, 11.22.

Compound 2a:

A mixture of 1-bromo-4-hexylbenzene (1.80g, 7.46 mmol) and THF (30 mL) was carefully degassed and cooled to -78 °C. *n*-BuLi (3.2 mL, 2.4 mol/L in hexane) was added dropwise to the solution, the mixture was stirred at this temperature for 1h, then quenched with a solution of compound 1a (1.0g, 1.49 mmol) in THF (20 mL). After being kept at -78 °C for 1h, the reaction was allowed to warm to room temperature and stirred overnight. Water was added to the solution, and the solution was extracted with ethyl acetate for three times. The combined organic layer was dried over $MgSO_4$ and filtered, the organic solvent was removed under reduced pressure. The crude product was directly used without further purification. The crude product was dissolved in anhydrous dichloromethane (50 mL). After being carefully degassed, a $BF_3 \cdot Et_2O$ (1 mL) solution was added. After being stirred for 1h, methanol was added to quench the reaction. The organic solvent was removed under reduced pressure, the residue was purified with chromatography on silica gel column with petrol ether to give compound 2a (750 mg) as a light yellow oil in a yield of 42%. ^{1}H NMR (500MHz, $CDCl_3$) δ: 7.12 (d, *J* = 6.85 Hz, 8H), 7.04 (d, *J* = 6.85 Hz, 8H), 6.72 (s, 2H), 2.53 (t, *J* = 6.60 Hz, 8H), 2.30 (t, *J* = 5.60 Hz, 4H), 1.54-1.59 (m, 12H), 1.08-1.22(m, 44H), 0.81-0.89 (m, 18H). The product was not stable, so ^{13}C-NMR was not obtained.

Compound 2b:

Compound 2b was synthesized according to the similar procedure of compound 2a (800 mg, 39%). ^{1}H NMR (500MHz, $(CD_3)_2CO$) δ: 7.16 (d, *J* = 7.05 Hz, 8H), 7.07 (d, *J* = 6.95 Hz, 8H), 6.41 (s, 2H), 3.94 (t, *J* = 5.00 Hz, 4H), 2.73-2.77 (m, 8H), 2.52-2.55 (m, 12H), 1.52-1.57 (m, 12H), 1.23-1.33 (m, 32H), 0.81-086 (m, 18H). The product was also unstable in atmosphere, and ^{13}C-NMR was not obtained.

Compound 3a:

$POCl_3$ (1 mL) was added dropwise to anhydrous DMF (10 mL) at 0°C, the mixture was stirred at this temperature for 30 min. The formed Vilsmeier reagent was added dropwise to a solution of compound 2 (600 mg) in 1,2-dichloromethane (30 mL) at 0 °C. After being refluxed overnight, the mixture was poured into ice water, neutralized with Na_2CO_3, and then extracted with dichloromethane. The combined organic layer was washed with saturated NaCl aqueous solution for three times. The separated organic layer was dried over anhydrous $MgSO_4$ and filtered. The organic layer was removed under reduced pressure, the residue was purified with chromatography on silica gel column with petrol ether/DCM (1:1) to give compound 3a (450 mg) as an orange solid in a yield of 72%. ^{1}H NMR (500MHz, $CDCl_3$) δ: 9.88 (s, 2H), 7.12 (d, *J*

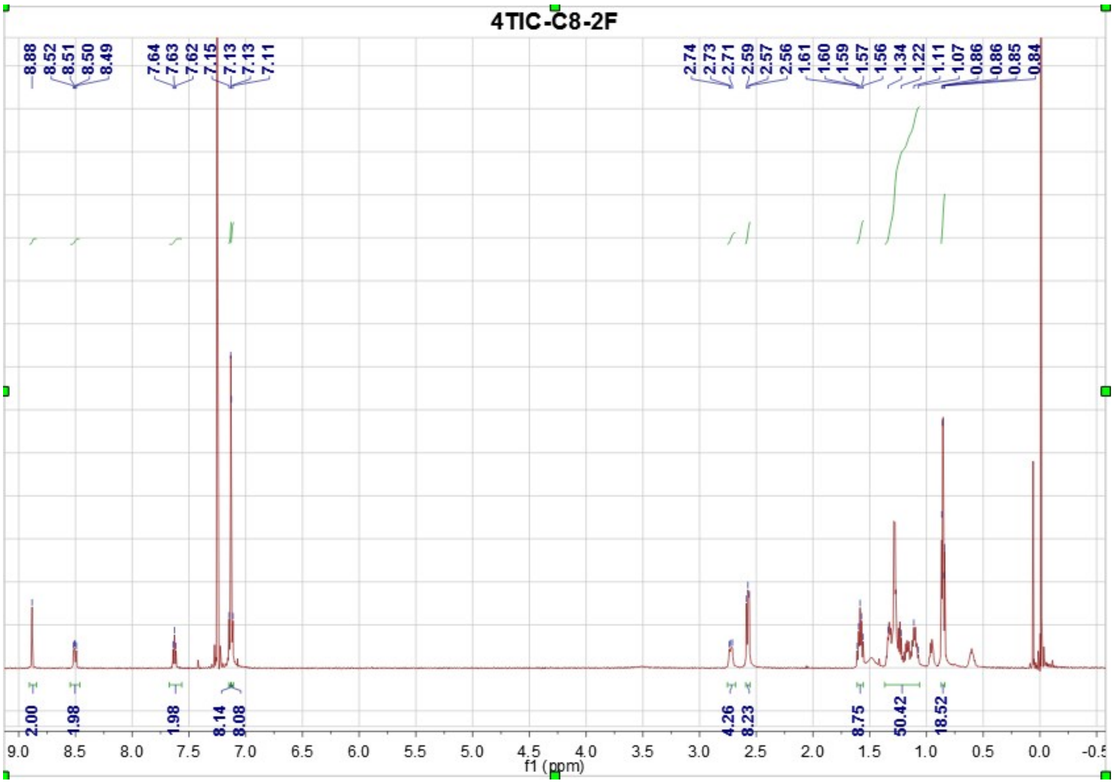
= 6.80 Hz, 8H), 7.09 (d, *J* = 6.90 Hz, 8H), 2.66 (t, *J* = 7.15 Hz, 4H), 2.56 (t, *J* = 6.35 Hz, 8H), 1.55-1.59 (m, 12H), 1.09-1.33 (m, 44H), 0.82-0.88 (m, 18H). ^{13}C NMR (125 MHz, CDCl3) δ: 181.62, 156.88, 154.49, 148.61, 147.05, 142.69, 138.57, 136.60, 135.87, 129.41, 128.74, 127.99, 35.59, 31.86, 31.28, 29.93, 29.36, 29.25, 29.16, 29.03, 28.42, 27.63, 22.60, 14.09.

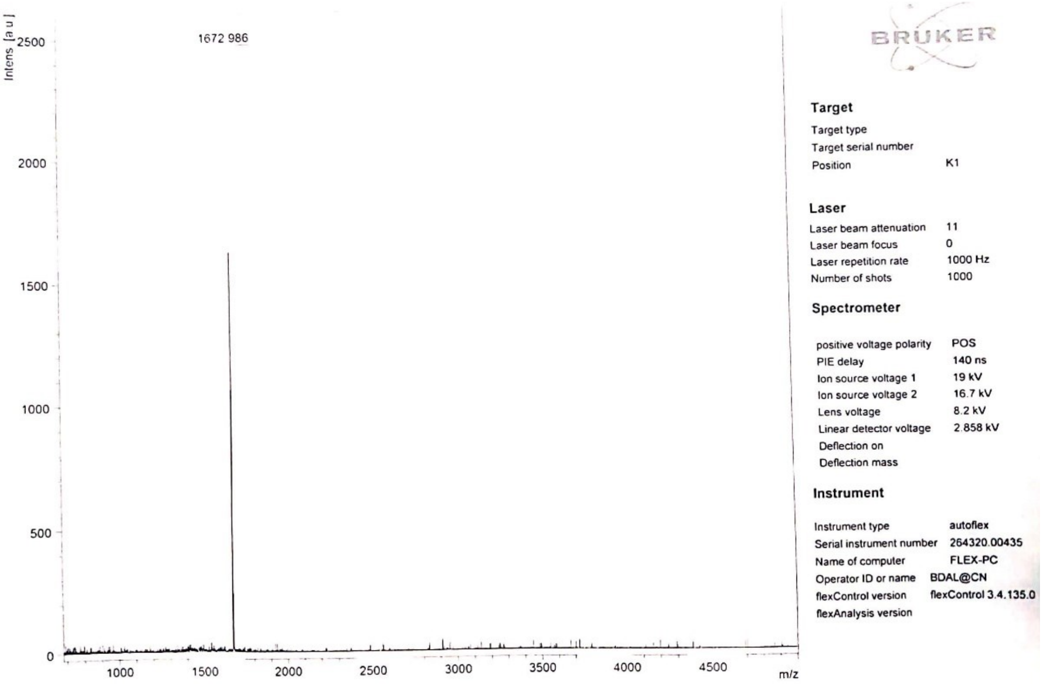
Compound 3b:

Compound 3b was synthesized according to the similar procedure of compound 3a (480 mg, 68%). ^{1}H NMR (500MHz, $CDCl_3$) δ: 9.95 (s, 2H), 7.13 (d, *J* = 8.2 Hz, 8H), 7.07(d, *J* = 8.2 Hz, 8H), 4.00 (t, *J* = 6.36 Hz, 4H), 2.55 (m, 8H), 1.53-1.58 (m, 12H), 1.18-1.33 (m, 44H), 0.81-0.86 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 182.42, 176.52, 148.71, 144.85, 142.66, 139.18, 138.14, 137.59, 136.42, 128.97, 127.75, 116.98, 70.45, 37.18, 35.62, 31.96, 31.26, 30.31, 29.73, 29.32, 29.18, 28.73, 27.12, 22.73, 22.58, 14.28.

4TIC-C8-2F:

A mixture of compound 3a (300 mg, 0.24 mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (280 mg, 1.22 mmol), and $CHCl_3$ (30 mL) was carefully degassed before and after the addition of 0.5 mL pyridine. After being stirred at room temperature overnight, the solvent was moved under reduced atmosphere. The residue was purified by chromatography on silica gel eluting with petrol ether/DCM (1:1, v/v) to give **4TIC-C8-2F** (243 mg) as a dark purple solid in a yield of 60%. ^{1}H NMR (500MHz, $CDCl_3$) δ: 8.88 (s, 2H), 8.50 (dd, *J* = 5.35, 8.25 Hz, 2H), 7.62 (t, *J* = 6.30 Hz, 2H), 7.13 (d, *J* = 7.35 Hz, 8H), 7.11 (d, *J* = 7.30 Hz, 8H), 2.73 (t, *J* = 6.50 Hz, 4H), 2.57 (t, *J* = 6.50 Hz, 8H), 1.56-1.61 (m, 8H), 1.08-1.34 (m, 48H), 0.84-0.87 (m, 18H). ^{13}C NMR (125 MHz, CDCl$_3$) δ: 186.15, 158.93, 157.84, 157.35, 155.93, 154.74, 153.06, 143.18, 140.70, 139.29, 136.40, 135.97, 134.95, 134.38, 128.97, 127.96, 118.99, 115.02, 114.91, 114.83, 114.73, 112.43, 112.28, 35.59, 31.90, 31.76, 31.69, 31.24, 30.26, 29.72, 29.48, 29.25, 29.16, 28.74, 22.67, 22.59, 14.13, 14.09. MS (MALDI-TOF): m/z 1672.986 (M$^+$)





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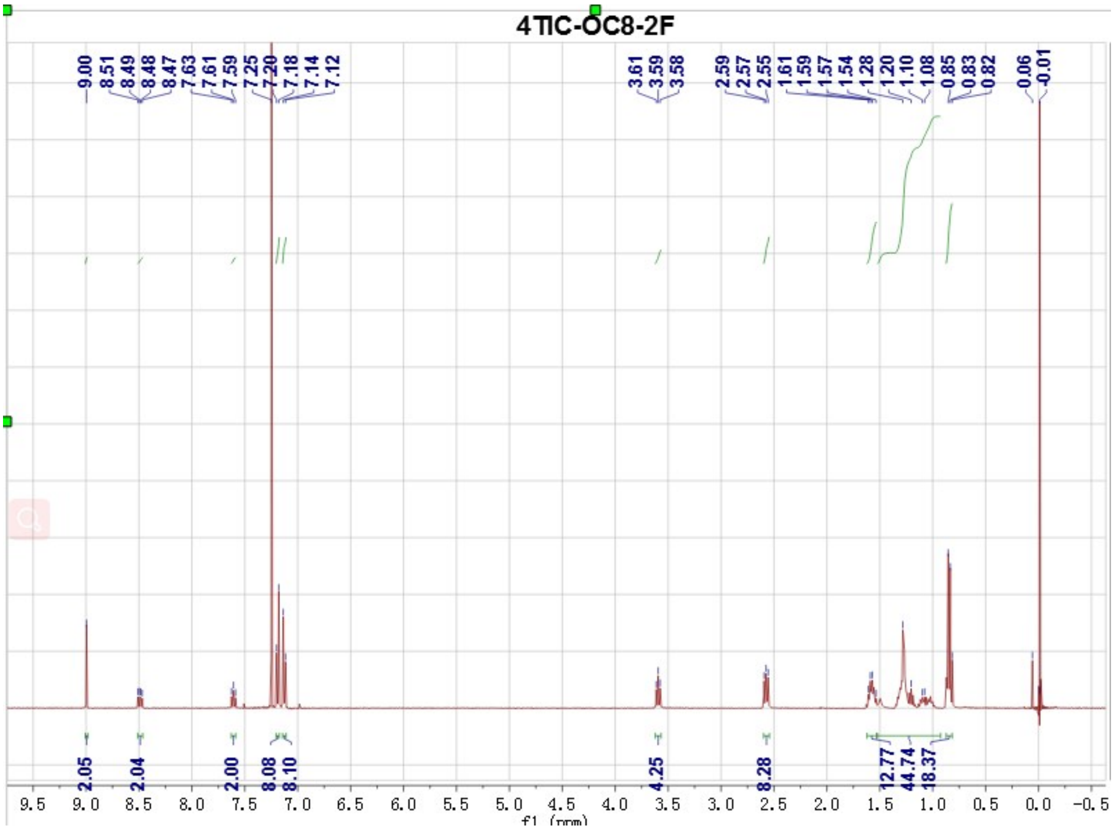
4TIC-OC8-2F:

Compound **4TIC-OC8-2F** was synthesized according to the similar procedure of **4TIC-C8-2F** (280 mg, 65%).^{1}H NMR (500MHz, $CDCl_3$) δ: 8.99 (s, 2H), 8.48 (dd, J = 6.56, 8.08 Hz, 2H), 7.61 (t, J = 7.68 Hz, 2H), 7.19 (d, *J* = 8.48 Hz, 8H), 7.12 (d, *J* = 8.52 Hz, 8H), 3.59 (t, *J* = 7.28 Hz, 4H), 2.57 (t, *J* = 7.60 Hz, 8H), 1.57-1.61 (m, 12H), 1.08-1.28 (m, 44H), 0.81-0.85 (m, 18H). ^{13}C NMR (125MHz, $CDCl_3$) δ: 186.42, 162.66, 158.69, 157.21, 156.18, 155.05, 152.97, 147.88, 143.25, 140.25, 139.78, 136.61, 135.15, 134.40, 134.23, 126.89, 118.24, 114.96, 114.59, 112.35, 35.56, 31.68, 31.37, 31.25, 29.34, 29.07, 24.79, 22.59, 22.55, 14.09, 13.99.MS (MALDI-TOF): m/z 1704.978 (M^+)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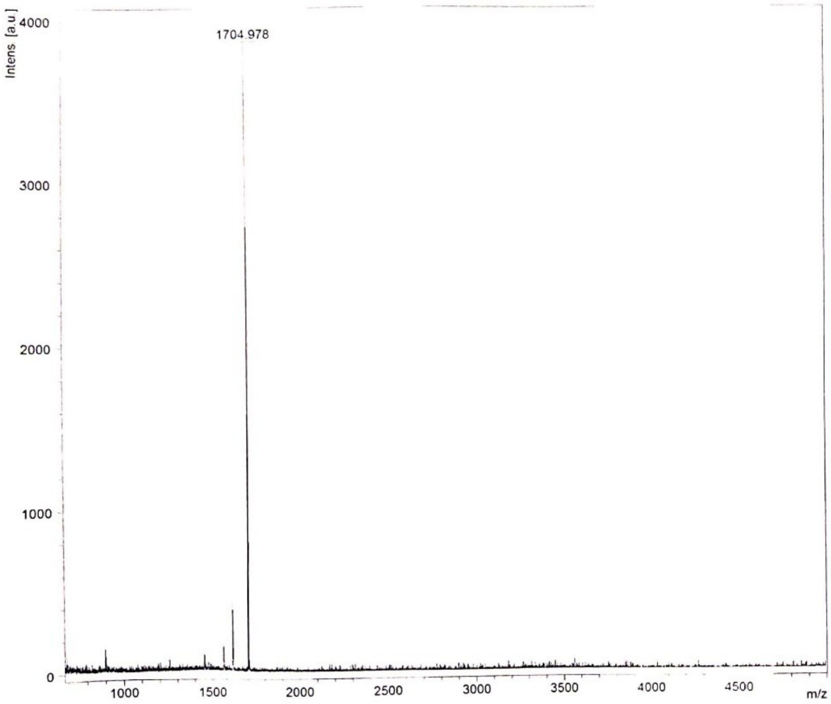

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Laser repetition rate	1000 Hz
Number of shots	2500

Spectrometer

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PIE delay	140 ns
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Ion source voltage 2	16.7 kV
Lens voltage	8.2 kV
Linear detector voltage	2.858 kV
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Instrument

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flexAnalysis version	