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Isomeric non fullerene acceptors for high efficiency organic solar cells

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Content

1. Measurements and Instruments

The ^{1}H, ^{13}C nuclear magnetic resonance (NMR) spectra were taken on a Bruker AV400 Spectrometer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker Autoflex III instrument. Fourier transform mass spectrometry (FTMS) with high-resolution matrix-assisted laser desorption/ionization (HR-MALDI) was performed on a Varian 7.0T FTMS instrument. Ultraviolet-visible (UV-*vis*) absorption spectra were measured on a UV-Vis instrument Agilent Cary 5000 UV-vis-NIR spectrophotometer. The cyclic voltammetry (CV) measurement was conducted by an electrochemical with three electrodes configuration, using calomel as the reference electrode, a Pt wire as the counter electrode, and a glassy carbon as the working electrode. 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile solution was used as the supporting electrolyte. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were calculated from the onset oxidation potential and the onset reduction potential. Potentials were calibrated with the ferrocene/ferrocenium (Fc/Fc^{+}) redox couple 4.8 eV relative to the vacuum level. The HOMO energy levels were determined by:

$$E_{HOMO} = -[q(E_{ox} - E_{ferrocene}) + 4.8]$$

while the LUMO energy levels were determined by:

$$E_{LUMO} = -[q(E_{re} - E_{ferrocene}) + 4.8]$$

The current density-voltage (J-V) curves of photovoltaic devices were recorded by a Keithley 2400 source-measure unit. The photocurrent was measured under the simulated illumination of 100 mW cm^{-2} with AM 1.5 G using a Enli SS-F5-3A solar simulator, which was calibrated by a standard Si solar cell (made by Enli Technology Co., Ltd., Taiwan, and calibrated report can be traced to NREL). The thickness of the active layers was measured by a Veeco Dektak 150 profilometer. The EQE spectra were measured by using a QE-R Solar Cell Spectral Response Measurement System (Enli Technology Co., Ltd., Taiwan). EQE_{EL} measurements were performed by applying external voltage/current sources through the devices (REPS, Enlitech). The FTPS-EQE measurement was carried out on an Enlitech FTPS PECT-600 instrument. Atomic force microscope (AFM) investigation was performed using Bruker MultiMode 8 in tapping mode. The transmission electron microscopy (TEM) investigation was performed on Philips Technical G2 F20 at 200 kV. The hole

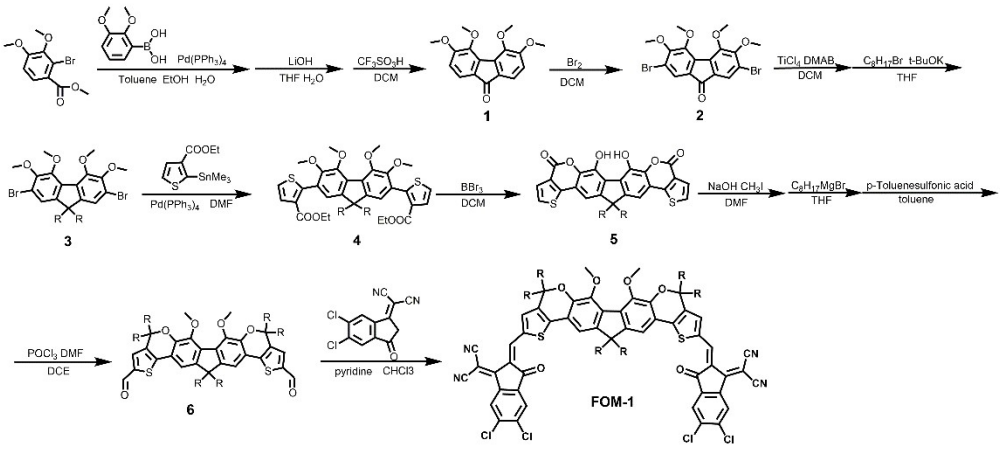
and electron mobility were measured using the space charge limited current (SCLC) method, employing a diode configuration of ITO/PEDOT:PSS/active layer/M_OO_3/Al for holes and ITO/ZnO/active layer/PDINO/Ag for electrons by taking the dark current density and fitting the results to a space charge limited form, where SCLC is described by:

$$J = \frac{9\varepsilon_0 \varepsilon_r \mu V^2}{8L^3}$$

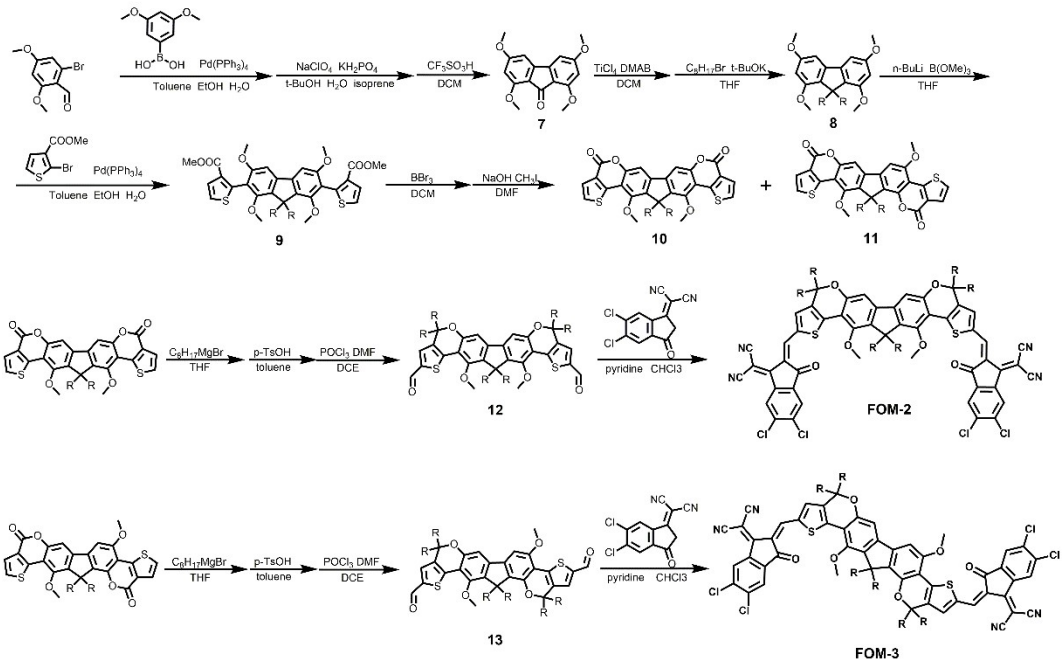
where J is the current density, L is the film thickness of the active layer, μ is the hole or electron mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), V ($=V_{appl} - V_{bi}$) is the internal voltage in the device, where V_{appl} is the applied voltage to the device and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes.

2. Materials Synthesis and Characterization

(a) Synthesis route of FOM-1



(b) Synthesis route of FOM-2 and FOM-3



Scheme S1. Synthetic route of FOM-1, FOM-2 and FOM-3.

Synthesis of compound 1

A mixture of methyl-2-bromo-3,4-dimethoxybenzoate (11.51 g, 42.01 mmol), 2,3-dimethoxybenzeneboronic acid (13.84 g, 76.01 mmol), potassium carbonate (15.72 g, 113.99 mmol), tetrakis(triphenylphosphine)palladium (2.40 g, 2.08 mmol), toluene (100 mL), ethanol (10 mL) and water (10 mL) were stirred at 100 ℃ under nitrogen. After stirring for 10 h, the mixture was allowed to cool and poured into water. The aqueous phase was extracted with ethyl acetate for three times. The organic phase was dried over sodium sulphate and concentrated under reduced

pressure.

Then the residue was mixed with tetrahydrofuran (75 mL), water (75 mL), methanol (75 mL) and lithium hydroxide (12.91 g, 53.91 mmol), and heat to 80 ℃. After stirring for 6 h, the mixture was allowed to cool and poured into water. The aqueous phase was extracted with ethyl acetate for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure.

Then the residue was mixed with dichloromethane (120 mL), after cooling to 0 ℃ under stirring, trifluoromethanesulfonic acid (11.5 mL) was added dropwise to the mixture. After stirring for 30 min, the mixture was added with freeze water and extracted with dichloromethane for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure. The residue was purified with column chromatography over silica gel to yield **1** as bright yellow solid (5.6g, 44%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 3.96 (s, 3H), 3.88 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 190.86, 160.09, 145.28, 134.77, 129.41, 121.27, 111.05, 62.43, 56.29.

Synthesis of compound 2

1 (3.01 g, 10mmol) was mixed with water (100 mL) and stirred at 0 ℃, bromine (2.8 mL) was added dropwise to the mixture. After stirring at 70 ℃ for 45 min, the mixture was allowed to cool down and poured into saturated sodium thiosulfate solution, The aqueous phase was extracted with dichloromethane for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure. The residue was recrystallization with chloroform and methanol to yield **2** as yellow solid (3.5 g, 77%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (s, 1H), 3.99 (s, 3H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.93, 150.32, 134.82, 131.47, 124.86, 118.72, 62.29, 60.99.

Synthesis of compound 3

A mixture of **2 (**3.5 g, 7.68 mmol**)**, dimethylamine-borane (1.31 g, 22.23 mmol), titanium tetrachloride (2.8 mL, 14.76 mmol) and dichloromethane (100 mL) were stirred at room temperature under nitrogen. After stirring for 30 min, the mixture was poured into water. The aqueous phase was extracted with dichloromethane for three times. The organic phase was dried over sodium

sulphate and concentrated under reduced pressure.

Then the residue was mixed with tetrahydrofuran (30 mL), 1-bromooctane (4.61 g, 23.87 mmol) and t-butoxide (3.95 g, 35.25 mmol), and stirred at room temperature. After stirring for 9 h, the mixture poured into water. The aqueous phase was extracted with ethyl acetate for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure. The residue was purified with column chromatography over silica gel to yield **3** as colorless oil (4.41 g, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 (s, 1H), 3.95 (s, 3H), 3.95 (s, 3H), 1.84 – 1.78 (m, 2H), 1.27 – 1.05 (m, 10H), 0.83 (t, *J* = 7.1 Hz, 3H), 0.56 (t, *J* = 6.3 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.50, 149.79, 148.48, 132.56, 121.87, 117.17, 62.01, 60.82, 54.62, 40.88, 31.75, 29.80, 29.19, 29.14, 23.40, 22.60, 14.06.

Synthesis of compound 4

A mixture of **3** (1.1 g, 1.65 mmol), ethyl 2-(trimethylstannyl)thiophene-3-carboxylate (2.20 g, 6.87 mmol), tetrakis(triphenylphosphine)palladium (0.35 g, 0.33 mmol) and N,N-Dimethylformamide (30 mL) were stirred at 100 ℃ under nitrogen. After stirring for 15 h, the mixture was allowed to cool and poured into water. The aqueous phase was extracted with ethyl acetate for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure. The residue was purified with column chromatography over silica gel to yield **4** as colorless oil (0.46 g, 35%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 5.4 Hz, 1H), 7.31 (d, *J* = 5.3 Hz, 1H), 6.99 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.97 (s, 3H), 3.71 (s, 3H), 1.93 – 1.81 (m, 2H), 1.20 – 1.03 (m, 13H), 0.81 (t, *J* = 7.0 Hz, 3H), 0.77 – 0.66 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.79, 151.07, 148.92, 147.32, 145.43, 133.67, 130.78, 129.27, 127.65, 124.43, 119.96, 61.88, 60.85, 60.31, 54.38, 40.86, 31.79, 29.93, 29.25, 29.22, 23.57, 22.59, 14.06, 13.93.

Synthesis of compound 5

4 (1.42 g, 1.74 mmol) was mixed with dichloromethane (20 mL) and stirred at 0 ℃, boron tribromide (20 mL, 1 M in dichloromethane) was added dropwise to the mixture. After stirring at room temperature for 6 h, the mixture was added with ice water slowly, the aqueous phase was extracted with dichloromethane for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure. The residue was recrystallization with chloroform and

methanol to yield **5** as yellow solid (0.95 g, 82%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.17 (s, 1H), 7.73 (d, *J* = 5.3 Hz, 1H), 7.48 (d, *J* = 5.2 Hz, 1H), 7.17 (s, 1H), 2.18 – 1.98 (m, 2H), 1.18 – 1.02 (m, 10H), 0.76 (t, *J* = 7.0 Hz, 3H), 0.62 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.02, 149.08, 148.06, 139.48, 138.16, 127.25, 127.21, 126.15, 125.16, 117.53, 108.39, 55.41, 41.58, 31.75, 29.81, 29.14, 23.62, 22.55, 14.02.

Synthesis of compound 6

5 (0.67 g, 1.00 mmol) was mixed with tetrahydrofuran (50 mL) and stirred at -78 ℃ under nitrogen, n-octylmagnesium bromide (10 mL, 2 M in ethyl ether) was added slowly to the mixture, then the mixture was warmed to room temperature slowly. After stirring at room temperature for 6 h, the mixture was added with ice water slowly, the aqueous phase was extracted with ethyl acetate for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure.

Then, the residue was added with toluene (30 mL) and p-toluenesulfonic acid (0.40 g, 2.15 mmol) and stirred at 100 ℃ under nitrogen, after 8 h, the mixture was allowed to cool and poured into water. The aqueous phase was extracted with ethyl acetate for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure.

After that, the residue was added with N,N-Dimethylformamide (30 mL), sodium hydroxide (0.50 g, 12.50 mmol), iodomethane (2.5 mL, 40.16 mmol) and stirred at 80 ℃ under nitrogen, after 8 h, the mixture was allowed to cool and poured into water. The aqueous phase was extracted with ethyl acetate for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure.

Then, the residue was added with dichloroethane (30 mL) and stirred at 0 ℃ under nitrogen, then a mixture of N,N-Dimethylformamide (2 mL) and phosphorus oxychloride (0.5 mL) was added slowly to the mixture, then the mixture was warmed to 90 ℃, after 12 h, the mixture was allowed to cool and poured into aqueous potassium acetate solution and stirred at room temperature for 2 h. Then, the aqueous phase was extracted with dichloromethane for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure. The residue was purified with column chromatography over silica gel to yield **6** as brown solid (0.37g, 32% in four steps). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.88 (s, 1H), 7.43 (s, 1H), 7.01 (s, 1H), 3.97 (s, 3H), 2.11 –

1.84 (m, 6H), 1.40 – 1.04 (m, 34H), 0.90 – 0.76 (m, 9H), 0.74 – 0.59 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.19, 146.40, 145.33, 144.75, 142.93, 141.09, 137.98, 135.07, 133.63, 118.42, 112.38, 83.81, 77.34, 77.03, 76.71, 61.86, 53.90, 41.15, 39.88, 31.81, 31.79, 29.89, 29.82, 29.47, 29.23, 29.20, 29.16, 23.87, 23.55, 22.63, 22.61, 14.08, 14.04.

Synthesis of FOM-1

6 (110 mg, 0.094 mmol) was mixed with 2-(5,6-dichloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (100 mg, 0.38 mmol), pyridine (0.5 mL) and chloroform (30 mL). The mixture was stirred at reflux for 12 h under nitrogen. After cooling down to room temperature, the mixture was poured into methanol (150 mL) and filtered. The residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (2:1) as eluent yielding a purple solid (105 mg, 76%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.91 (s, 1H), 8.81 (s, 1H), 7.99 (s, 1H), 7.51 (s, 1H), 7.22 (s, 1H), 3.99 (s, 3H), 2.05 (td, *J* = 13.1, 12.1, 4.7 Hz, 2H), 2.01 – 1.87 (m, 4H), 1.38 – 1.08 (m, 34H), 0.84 (t, *J* = 6.9 Hz, 6H), 0.76 (t, *J* = 6.9 Hz, 3H), 0.66 (dq, *J* = 12.0, 7.3, 5.6 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 186.53, 158.18, 151.62, 147.84, 146.10, 144.99, 142.91, 139.92, 139.68, 139.59, 138.71, 138.34, 136.59, 136.00, 135.92, 127.08, 125.19, 120.96, 118.81, 114.36, 114.24, 113.09, 84.02, 69.80, 61.92, 41.33, 40.27, 31.79, 29.85, 29.80, 29.71, 29.46, 29.26, 29.23, 23.82, 23.65, 22.64, 22.62, 14.09, 14.07. HR-MS: calculated for $C_{99}H_{118}Cl_4N_4O_6S_2$ $[M]^+$, 1665.98; found: 1665.73.

Synthesis of compound 7

A mixture of 2-Bromo-4,6-dimethoxybenzaldehyde (12.20 g, 50.00 mmol), 3,5-bimethoxybenzeneboronic acid (10.17 g, 55.85 mmol), potassium carbonate (18.12 g, 131.4 mmol), tetrakis(triphenylphosphine)palladium (1.15 g, 1.00 mmol), toluene (100 mL), ethanol (20 mL) and water (20 mL) were stirred at 100 ℃ under nitrogen. After stirring for 10 h, the mixture was allowed to cool and poured into water. The aqueous phase was extracted with ethyl acetate for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure.

Then the residue was mixed with tert-butanol (160 mL), water (32 mL) and isopentane (32.5 mL), and stirred at room temperature, then sodium chlorite (18.54 g, 205.00 mmol) and potassium dihydrogen phosphate (10.42 g, 76.57 mmol) were added slowly to the mixture. After stirring for

30 min, dliute hydrochloric acid (100 mL, 2 M in water) was added slowly to the mixture, and stirred for further 1 h. Then, the aqueous phase was extracted with ethyl acetate for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure.

Then the residue was mixed with dichloromethane (100 mL), after cooling to 0 ℃ under stirring, trifluoromethanesulfonic acid (13.0 mL) was added dropwise to the mixture. After stirring for 30 min, the mixture was added with freeze water and extracted with dichloromethane for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure. The residue was recrystallization from chloroform to yield **7** as yellow solid (6.81 g, 52% in three steps). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.61 (t, *J* = 1.7 Hz, 1H), 6.27 (t, *J* = 1.6 Hz, 1H), 3.92 (s, 3H), 3.88 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.11, 166.05, 159.27, 146.56, 115.03, 99.21, 98.82, 56.11, 55.79.

Synthesis of compound 8

A mixture of **7** (3.01 g, 10.00 mmol), dimethylamine-borane (1.31 g, 22.23 mmol), titanium tetrachloride (2.8 mL, 14.76 mmol) and dichloromethane (100 mL) were stirred at room temperature under nitrogen. After stirring for 30 min, the mixture was poured into water. The aqueous phase was extracted with dichloromethane for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure.

Then the residue was mixed with tetrahydrofuran (120 mL), 1-bromooctane (4.50 g, 23.30 mmol) and potassium t-butoxide (4.00 g, 32.73 mmol), and stirred at room temperature. After stirring for 9 h, the mixture poured into water. The aqueous phase was extracted with ethyl acetate for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure. The residue was purified with column chromatography over silica gel to yield **8** as white solid (1.91 g, 38% in two steps). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.77 (d, *J* = 2.1 Hz, 1H), 6.37 (d, *J* = 2.1 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 2.27 – 2.19 (m, 2H), 1.26 – 1.01 (m, 10H), 0.82 (t, *J* = 7.1 Hz, 3H), 0.47 (dd, *J* = 10.8, 5.4 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.52, 157.05, 143.33, 130.30, 97.94, 95.74, 56.85, 55.43, 55.19, 34.80, 31.93, 29.94, 29.24, 29.21, 24.14, 22.69, 14.14.

Synthesis of compound 9

8 (1.90 g, 3.72 mmol) was mixed with tetrahydrofuran (30 mL) and stirred at 0 ℃ under nitrogen, n-butyllithium (4.90 mL, 1.6 M in n-Hexane) was added slowly to the mixture, after stirring at 0 ℃ for 4 h, the mixture was further cool down to -78 ℃, then trimethyl borate (1.54 g, 14.82 mmol) was added slowly to the mixture, after stirring at -78 ℃ for 30 min, the mixture was allowed to warm to room temperature and poured into water The aqueous phase was extracted with ethyl acetate for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure. The residue was then mixed with methyl 2-bromothiophene-3-carboxylate (2.80 g, 11.97 mmol), potassium carbonate (4.25 g, 30.82 mmol), tetrakis(triphenylphosphine)palladium (1.15 g, 1.00 mmol), toluene (50 mL), ethanol (10 mL) and water (10 mL), and stirred at 100 ℃ under nitrogen. After stirring for 10 h, the mixture was allowed to cool and poured into water. The aqueous phase was extracted with ethyl acetate for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure. The residue was purified with column chromatography over silica gel to yield **9** as yellow oil (1.56 g, 51% in two steps). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 5.3 Hz, 1H), 7.40 (d, *J* = 5.4 Hz, 1H), 7.01 (s, 1H), 3.85 (s, 3H), 3.65 (s, 3H), 3.36 (s, 3H), 2.28 (t, *J* = 8.4 Hz, 2H), 1.24 – 1.09 (m, 10H), 0.81 (t, *J* = 7.0 Hz, 3H), 0.68 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.50, 158.03, 155.52, 143.21, 141.71, 134.12, 131.92, 128.61, 125.59, 115.40, 97.63, 60.09, 59.85, 57.74, 55.98, 31.85, 29.34, 24.38, 22.63, 14.13, 14.09.

Synthesis of 10 and 11

9 (0.72 g, 0.88 mmol) was mixed with dichloromethane (50 mL) and stirred at 0 ℃, boron tribromide was added dropwise to the mixture. After stirring at room temperature for 6 h, the mixture was added with ice water slowly, the aqueous phase was extracted with dichloromethane for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure. The residue was recrystallization with chloroform and methanol to obtain a yellow solid, without further purification, the residue was mixed with N,N-Dimethylformamide (20 mL), potassium carbonate (0.90 g, 6.52 mmol) and iodomethane (1.5 mL, 24.09 mmol), and heated to 50 ℃ under nitrogen, after stirring for 6 h, the mixture was allowed to cool down and poured into water. The aqueous phase was extracted with ethyl acetate for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure. The residue was purified with column

chromatography over silica gel to yield **10** (0.38 g, 62%) and **11** (0.13 g, 21%) as yellow solid.

Spectrum of 10: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 5.4 Hz, 1H), 7.58 (s, 1H), 7.53 (d, *J* = 5.4 Hz, 1H), 4.01 (s, 3H), 2.56 – 2.46 (m, 2H), 1.16 – 0.96 (m, 10H), 0.74 (t, *J* = 6.9 Hz, 3H), 0.62 (q, *J* = 7.9, 7.3 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.27, 152.57, 151.68, 143.55, 142.61, 137.74, 127.77, 126.12, 124.91, 113.13, 105.60, 62.44, 58.95, 37.62, 31.70, 29.59, 29.22, 29.12, 24.30, 22.52, 14.01.

Spectrum of 11: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 5.4 Hz, 1H), 7.71 (d, *J* = 5.4 Hz, 1H), 7.65 (s, 1H), 7.52 (d, *J* = 5.3 Hz, 1H), 7.46 (d, *J* = 5.3 Hz, 1H), 4.22 (s, 3H), 4.03 (s, 3H), 2.78 (td, *J* = 12.7, 12.1, 5.1 Hz, 2H), 2.47 (td, *J* = 13.3, 12.7, 4.9 Hz, 2H), 1.12 – 0.96 (m, 20H), 0.70 (t, *J* = 6.9 Hz, 6H), 0.57 (ddq, *J* = 19.7, 12.6, 7.1, 6.6 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.41, 157.11, 155.26, 152.50, 151.80, 147.84, 145.07, 143.82, 143.60, 141.61, 138.41, 128.97, 127.74, 127.54, 125.95, 125.70, 124.70, 123.52, 112.65, 108.69, 105.32, 97.78, 62.38, 58.60, 56.40, 36.47, 31.70, 29.56, 29.19, 29.10, 24.36, 22.52, 13.98.

Synthesis of compound 12

10 (0.70 g, 1.00 mmol) was mixed with tetrahydrofuran (30 mL) and stirred at -78 ℃ under nitrogen, n-octylmagnesium bromide (5 mL, 2 M in ethyl ether) was added slowly to the mixture, then the mixture was warmed to room temperature slowly. After stirring at room temperature for 6 h, the mixture was added with ice water slowly, the aqueous phase was extracted with ethyl acetate for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure.

Then, the residue was added with toluene (30 mL) and p-Toluenesulfonic acid (0.40 g, 2.15 mmol) and stirred at 100 ℃ under nitrogen, after 8 h, the mixture was allowed to cool and poured into water. The aqueous phase was extracted with ethyl acetate for three times. The organic phase was dried over sodium sulphate and concentrated under reduced pressure.

Then, the residue was added with dichloroethane (30 mL) and stirred at 0 ℃ under nitrogen, then a mixture of N,N-Dimethylformamide (2 mL) and phosphorus oxychloride (0.5 mL) was added slowly to the mixture, then the mixture was warmed to 90 ℃, after 12 h, the mixture was allowed to cool and poured into aqueous Potassium acetate solution and stirred at room temperature for 1 h. Then, the aqueous phase was extracted with dichloromethane for three times. The organic phase

was dried over sodium sulphate and concentrated under reduced pressure. The residue was purified with column chromatography over silica gel to yield **12** as brown solid (0. 68g, 58% in three steps). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.91 (s, 1H), 7.43 (s, 1H), 7.00 (s, 1H), 3.86 (s, 3H), 2.44 – 2.32 (m, 2H), 2.01 – 1.86 (m, 4H), 1.70 – 1.59 (m, 2H), 1.25 – 1.01 (m, 28H), 0.88 – 0.83 (m, 10H), 0.77 (t, *J* = 6.8 Hz, 3H), 0.73 – 0.62 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.79, 154.34, 152.79, 144.18, 142.03, 138.15, 137.96, 134.77, 132.28, 112.88, 104.85, 82.77, 62.01, 58.14, 39.48, 35.43, 31.84, 31.76, 29.89, 29.72, 29.68, 29.46, 29.27, 29.23, 24.25, 23.79, 22.65, 22.61, 14.09, 14.04.

Synthesis of compound 13

Compound **13** was prepared following the same procedure as for **12**. The product was afforded as a brown solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.92 (s, 1H), 9.90 (s, 1H), 7.45 (s, 1H), 7.42 (s, 1H), 7.08 (s, 1H), 6.79 (s, 1H), 4.06 (s, 3H), 3.87 (s, 3H), 2.53 – 2.42 (m, 2H), 2.30 (ddd, *J* = 16.2, 8.7, 5.2 Hz, 2H), 2.07 – 1.90 (m, 8H), 1.26 – 1.16 (m, 42H), 1.13 – 1.03 (m, 18H), 0.85 (td, *J* = 8.1, 7.1, 2.8 Hz, 19H), 0.77 (t, *J* = 7.0 Hz, 6H), 0.65 (p, *J* = 8.3, 7.9 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.93, 182.74, 155.76, 154.28, 152.92, 149.69, 144.88, 143.33, 141.99, 141.18, 139.01, 138.25, 137.82, 135.23, 135.17, 132.32, 128.69, 112.58, 107.46, 104.75, 94.65, 83.79, 82.73, 61.96, 57.65, 55.67, 41.03, 39.50, 36.59, 31.88, 31.85, 30.22, 30.08, 29.93, 29.74, 29.66, 29.62, 29.48, 29.40, 29.25, 24.54, 23.95, 23.81, 22.67, 22.65, 14.10, 14.05.

Synthesis of FOM-2

Compound **FOM-2** was prepared following the same procedure as for **FOM-1**. The product was afforded as a purple solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.88 (s, 1H), 8.77 (s, 1H), 7.98 (s, 1H), 7.62 (s, 1H), 7.06 (s, 1H), 4.00 (s, 3H), 2.51 – 2.41 (m, 2H), 1.97 (dhept, *J* = 14.6, 6.1 Hz, 4H), 1.44 – 1.19 (m, 25H), 1.16 – 1.04 (m, 9H), 0.84 (t, *J* = 6.6 Hz, 6H), 0.75 (t, *J* = 6.7 Hz, 3H), 0.73 – 0.66 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 185.81, 158.41, 155.53, 153.43, 147.41, 145.73, 141.26, 139.91, 139.62, 139.43, 138.62, 138.29, 137.48, 136.07, 135.47, 126.93, 125.21, 121.15, 114.45, 114.37, 113.91, 105.33, 83.01, 69.40, 62.22, 58.34, 39.85, 37.72, 31.84, 31.78, 29.83, 29.77, 29.47, 29.27, 29.24, 24.48, 23.80, 22.66, 22.62, 14.11, 14.08. HR-MS: calculated for $C_{99}H_{118}Cl_4N_4O_6S_2$ $[M]^+$, 1665.98; found: 1665.73.

Synthesis of FOM-3

Compound **FOM-3** was prepared following the same procedure as for **FOM-1**. The product was afforded as a purple solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.89 (s, 1H), 8.85 (s, 1H), 8.79 (s, 1H), 8.77 (s, 1H), 8.00 (s, 1H), 7.98 (s, 1H), 7.68 (s, 1H), 7.62 (s, 1H), 7.12 (s, 1H), 6.84 (s, 1H), 4.20 (s, 3H), 3.98 (s, 3H), 2.48 (td, *J* = 11.7, 10.5, 6.0 Hz, 2H), 2.39 – 2.29 (m, 2H), 2.04 (ddd, *J* = 15.3, 11.1, 4.4 Hz, 2H), 1.97 (dt, *J* = 9.7, 4.4 Hz, 6H), 1.40 – 1.20 (m, 48H), 1.17 – 1.03 (m, 20H), 0.84 (t, *J* = 7.0 Hz, 12H), 0.76 (t, *J* = 7.1 Hz, 6H), 0.71 – 0.60 (m, 4H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 185.91, 158.77, 158.55, 156.92, 155.44, 153.51, 148.89, 147.44, 146.37, 145.05, 141.20, 139.77, 139.61, 139.42, 139.31, 139.14, 138.65, 138.32, 138.26, 137.70, 137.41, 136.94, 136.14, 136.10, 135.92, 129.14, 126.96, 126.86, 125.23, 125.08, 121.17, 120.63, 114.70, 114.63, 114.48, 114.40, 113.61, 105.21, 95.00, 84.01, 82.97, 69.34, 68.53, 62.14, 57.82, 56.13, 41.31, 39.83, 36.58, 31.86, 31.83, 30.22, 30.00, 29.84, 29.74, 29.60, 29.49, 29.46, 29.40, 29.23, 24.68, 23.92, 23.80, 22.66, 22.64, 14.10, 14.04. HR-MS: calculated for $C_{99}H_{118}Cl_4N_4O_6S_2$ $[M]^+$, 1665.98; found: 1665.73.

3. Device Fabrication

The OSCs were fabricated by applying an inverted architecture of ITO/ZnO/NMA/active layer/MoO_3/Ag. Firstly, the indium tin oxide (ITO) glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol in turn for 15 min and subsequently dried by use of an argon blow. Subsequently, the ZnO was deposited by spin-coating a ZnO precursor solution on the top of ITO glass substrates at 3000 rpm for 20 s. After being baked at 200 °C in the air for 40 min, the ZnO-coated substrates were transferred into an argon-filled glove box. In order to fine-tune the interfacial properties, a thin film of cathode interface modification layer was spin-coated on ZnO. Subsequently, the PM6/FOMs in chlorobenzene (CB) with DIO additive contents was spin-coated onto the cathode interface modification layer. Then, MoO_3 (~6 nm) and Ag (~150 nm) were successively evaporated onto the active layer through a shadow mask ($2x10^4$ Pa). The effective area for the devices is 4 mm^2.

Table S1. Photovoltaic performance of the solar cells based on **PM6**:**FOM-1** with different D:A ratios under the illumination of AM 1.5G, 100 mW cm^{-2}.

D/A [w/w]	V_{OC} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
1:1.0	0.878	20.49	71.27	12.86
1:1.2	0.878	21.16	70.20	13.03
1:1.4	0.873	21.01	70.15	12.86

Table S2. Photovoltaic performance of the solar cells based on **PM6**:**FOM-1** (1:1.2, w/w) with different DIO contents under the illumination of AM 1.5G, 100 mW cm^{-2}.

V%	V_{OC} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
0.1	0.860	21.43	72.45	13.37
0.3	0.853	21.67	73.47	13.60
0.5	0.847	20.66	70.36	12.33

Table S3. Photovoltaic performances of the solar cells based on **PM6**:**FOM-1** (1:1.2, w/w, 0.3% DIO) with different thermal annealing temperature under one sun illumination (AM 1.5G, 100 mW cm^{-2}).

Thermal annealing (TA) [℃]	V_{OC} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
None	0.881	21.40	74.17	13.99
60	0.863	21.70	75.17	14.07
80	0.862	21.49	74.70	13.83

Table S4 Photovoltaic performances of the solar cells based on **PM6**:**FOM-1** (1:1.2, w/w, 0.3% DIO, 60 ℃ annealing) with different cathode interface modification layer under one sun illumination (AM 1.5G, 100 mW cm^{-2}).

cathode interface modification layer	V_{OC} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
PFN-Br	0.863	21.70	75.17	14.07
NMA	0.864	22.16	74.88	14.34

Table S5. Photovoltaic performance of the solar cells based on **PM6**:**FOM-2** with different D:A ratios under the illumination of AM 1.5G, 100 mW cm^{-2}.

D/A [w/w]	V_{OC} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
1:0.8	0.931	18.92	70.74	12.46
1:1.0	0.913	19.83	70.21	12.68
1:1.2	0.903	19.91	67.92	12.23

Table S6. Photovoltaic performance of the solar cells based on **PM6**:**FOM-2** (1:1.0, w/w) with different DIO contents under the illumination of AM 1.5G, 100 mW cm^{-2}.

V%	V_{OC} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
0.1	0.916	19.39	72.07	12.84
0.3	0.905	20.04	74.00	13.44
0.5	0.857	18.20	64.39	10.07

Table S7. Photovoltaic performances of the solar cells based on **PM6**:**FOM-2** (1:1.0, w/w, 0.3% DIO) with different thermal annealing temperature under one sun illumination (AM 1.5G, 100 mW cm^{-2}).

Thermal annealing (TA) [℃]	V_{OC} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
60	0.906	21.03	73.27	14.01
80	0.904	21.02	75.45	14.38
100	0.896	21.27	74.52	14.26

Table S8 Photovoltaic performances of the solar cells based on **PM6**:**FOM-2** (1:1.0, w/w, 0.3% DIO, 80 ℃ annealing) with different cathode interface modification layer under one sun illumination (AM 1.5G, 100 mW cm^{-2}).

cathode interface modification layer	V_{OC} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
PFN-Br	0.904	21.02	75.45	14.38
NMA	0.904	21.38	76.59	15.10

Table S9. Photovoltaic performance of the solar cells based on **PM6**:**FOM-3** with different D:A ratios under the illumination of AM 1.5G, 100 mW cm^{-2}.

D/A [w/w]	V_{OC} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
1:0.8	0.949	19.08	71.40	12.94
1:1.0	0.951	19.41	72.95	13.47
1:1.2	0.932	19.64	69.80	12.79

Table S10. Photovoltaic performance of the solar cells based on **PM6**:**FOM-3** (1:1.0, w/w) with different DIO contents under the illumination of AM 1.5G, 100 mW cm^{-2}.

V%	V_{OC} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
0.3	0.912	19.65	72.76	13.04
0.5	0.933	20.19	74.31	14.01
0.7	0.938	20.30	72.74	13.87

Table S11. Photovoltaic performances of the solar cells based on **PM6**:**FOM-3** (1:1.0, w/w, 0.5% DIO) with different thermal annealing temperature under one sun illumination (AM 1.5G, 100 mW cm^{-2}).

Thermal annealing (TA) [℃]	V_{OC} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
none	0.933	20.19	74.31	14.01
60	0.935	20.38	75.07	14.27
80	0.925	19.90	74.09	13.67

Table S12. Photovoltaic performances of the solar cells based on **PM6**:**FOM-3** (1:1.0, w/w, 0.5% DIO, 60 ℃ annealing) with different cathode interface modification layer under one sun illumination (AM 1.5G, 100 mW cm^{-2}).

cathode interface modification layer	V_{OC} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
PFN-Br	0.935	20.38	75.07	14.27
NMA	0.939	21.06	75.89	15.02

4. The calculation method of E_{loss}

E_{loss} can be calculated by the equation:

$$E_{loss} = E_g - qV_{oc}$$

Where E_g can be calculated by the crossing point of normalized absorption and photoluminescence spectra.

The detailed components of E_{loss} can be categorized into three parts based on the Shockley-Queisser (SQ) limit[2-4]:

$$E_{loss} = (E_g - qV_{oc}^{SQ}) + (qV_{oc}^{SQ} - qV_{oc}^{rad}) + (qV_{oc}^{rad} - qV_{oc})$$

Where

$$V_{oc}^{SQ} = \frac{kT}{q}\ln\left(\frac{J_{sc}^{SQ}}{J_0^{SQ}} + 1\right) \cong \frac{kT}{q}\ln\left(\frac{q \cdot \int_{E_g}^{+\infty} \emptyset_{AM1.5G}(E)dE}{q \cdot \int_{E_g}^{+\infty} \emptyset_{BB}(E)dE}\right)$$

Where $\emptyset_{BB}(E)$ is black body emission at room temperature. Thus, for the unavoidable radiative recombination ΔE_1:

$$\Delta E_1 = E_g - qV_{oc}^{SQ}$$

$$V_{oc}^{rad} = \frac{kT}{q}\ln\left(\frac{J_{sc}}{J_0^{rad}} + 1\right) \cong \frac{kT}{q}\ln\left(\frac{q \cdot \int_0^{+\infty} EQE(E)\emptyset_{AM1.5G}(E)dE}{q \cdot \int_0^{+\infty} EQE(E)\emptyset_{BB}(E)dE}\right)$$

Thus, for the radiative recombination ΔE_2

$$\Delta E_2 = qV_{oc}^{SQ} - qV_{oc}^{rad}$$

Finally, for the non-radiative recombination loss ΔE_3

$$\Delta E_3 = qV_{oc}^{rad} - qV_{oc}$$

Where V_{OC} is the open circuit voltage of the OSC.

5. Figures and Tables

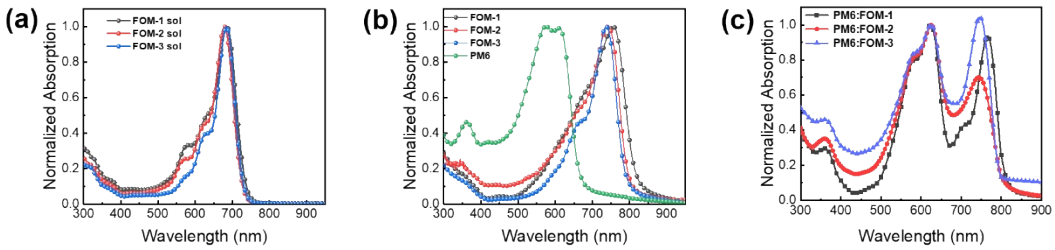


Figure S1. Normalized absorption of FOM-1, FOM-2 and FOM-3, (a) in chloroform, (b) on the neat films, (c) blending film absorptions of the three acceptors with PM6 under optimized conditions.

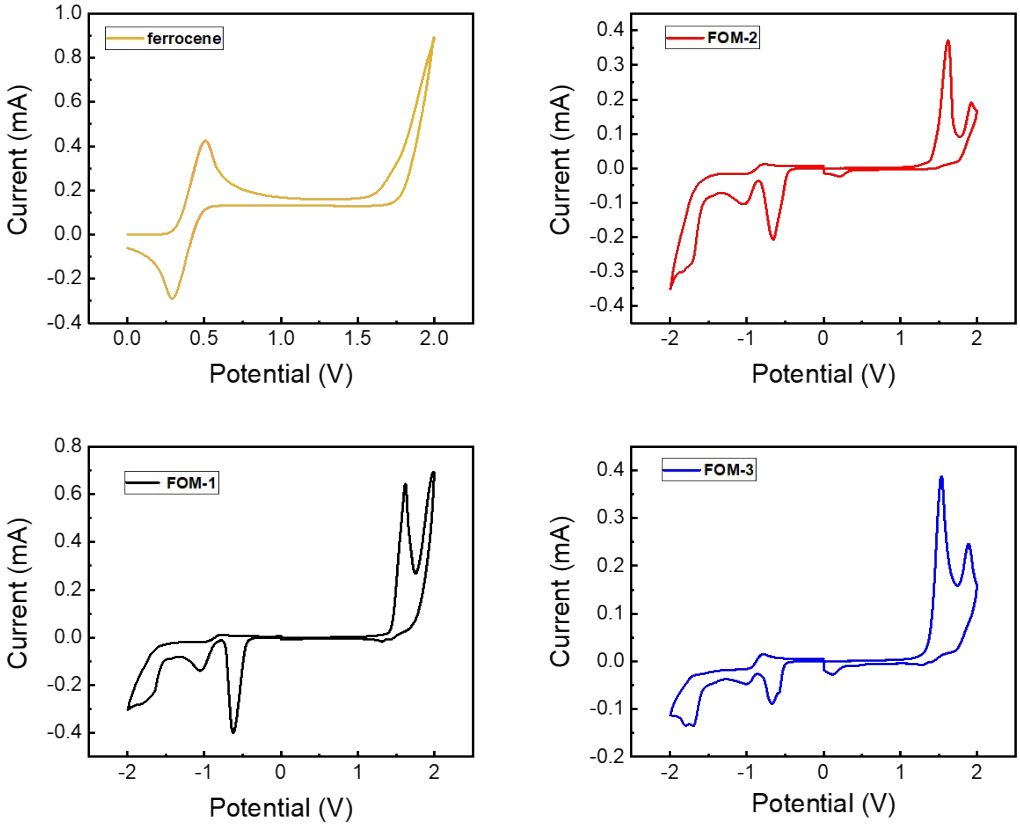


Figure S2. Cyclic voltammetry plots of **FOMs** film.

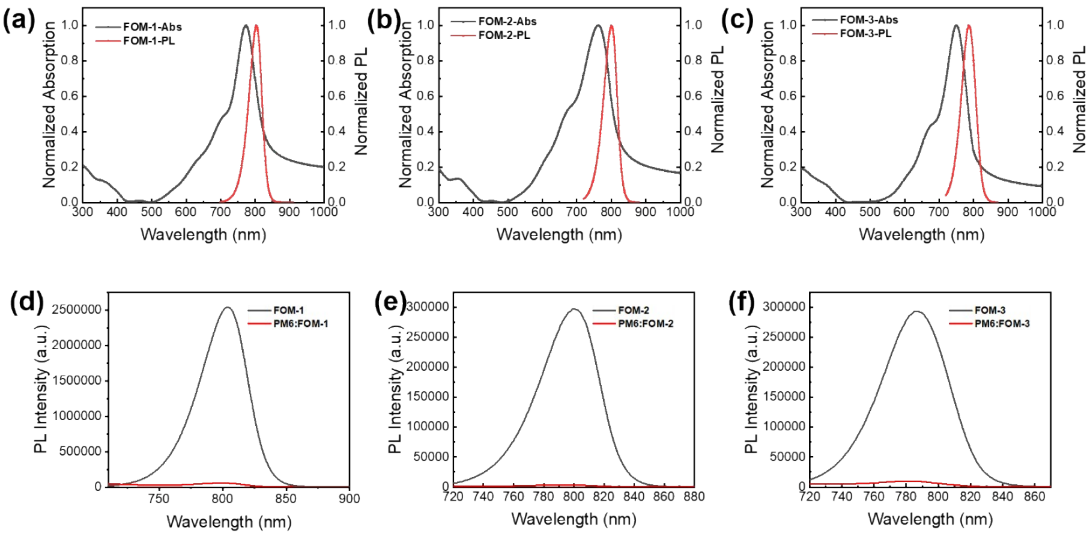


Figure S3. (a-c) Normalized absorption and PL spectra of FOM series films, (d-f) PL spectra of FOM series films and their blend films with PM6.

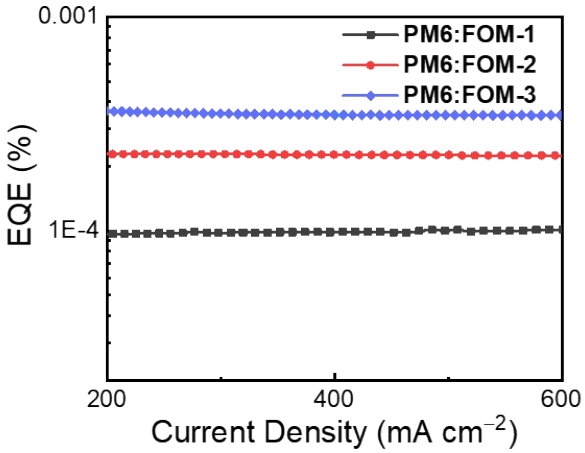


Figure S4. EQE_{EL} spectra of PM6:FOM series OSCs.

Table S13. Summary of the GIWAXS parameters for the neat acceptor films and blend films.

film	q (010, Å^{-1})	d-spacing[a] (010, Å^{-1})	FWHM (010, Å^{-1})	CCL[b] (010, Å^{-1})	q (100, Å^{-1})	d-spacing[a] (100, Å^{-1})
FOM-1	1.81	3.47	0.121	46.79	0.325	19.35
FOM-2	1.78	3.52	0.265	21.34	0.313	20.10
FOM-3	1.82	3.45	0.164	34.52	0.300	20.91
PM6:FOM-1	1.78	3.54	0.182	31.07	0.329	19.12
PM6:FOM-2	1.80	3.49	0.195	28.95	0.317	19.85
PM6:FOM-3	1.73	3.63	0.234	24.16	0.309	20.37

6. NMR and HR-MS Spectra

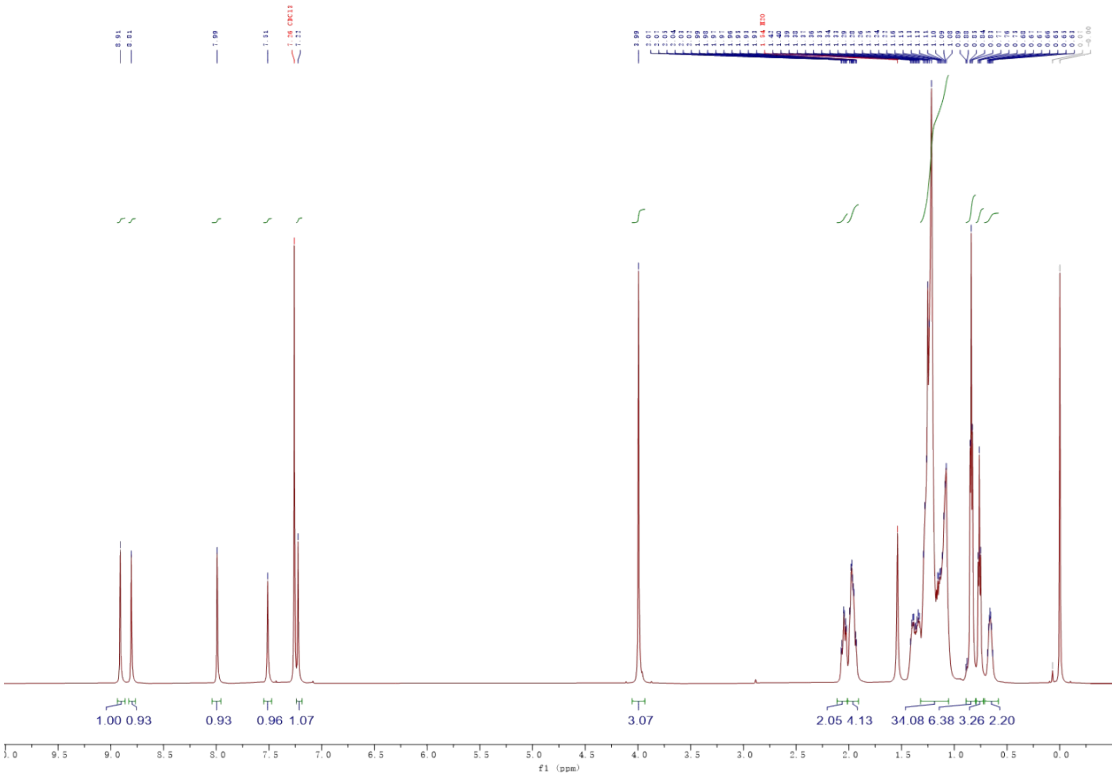


Figure S5. ^{1}H NMR (600 MHz) of compound **FOM-1**.

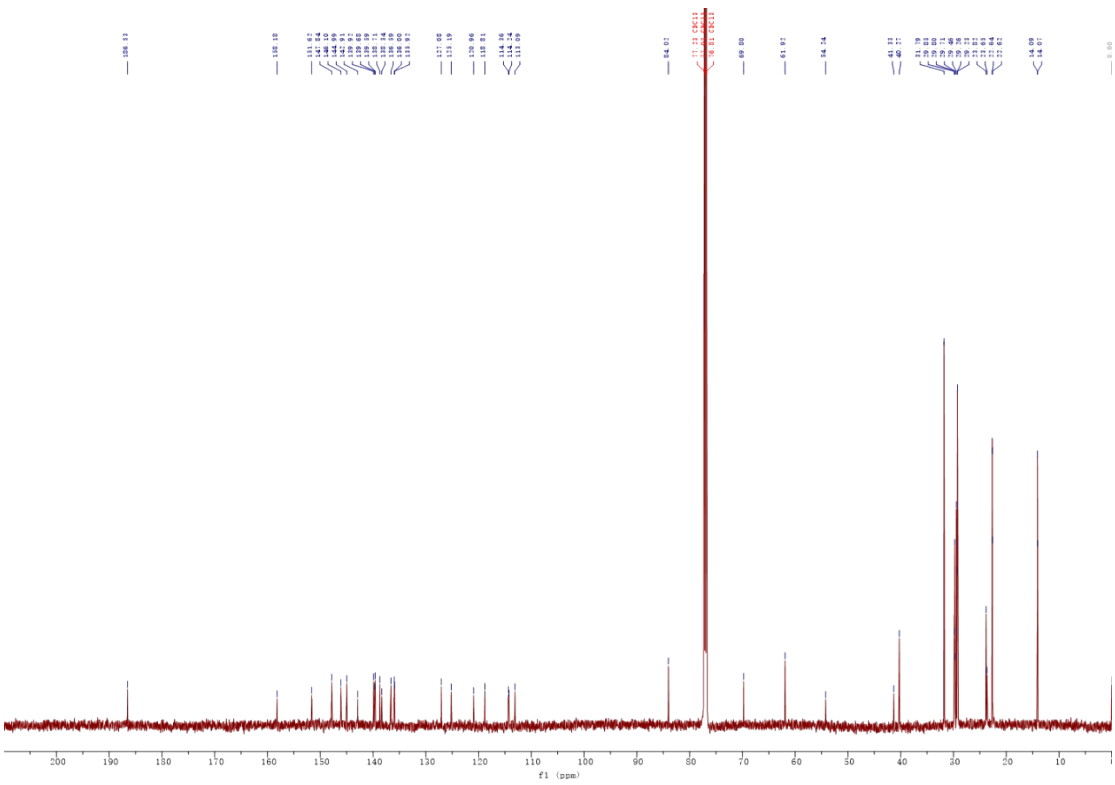


Figure S6. ^{13}C NMR (151 MHz) of compound**FOM-1**.

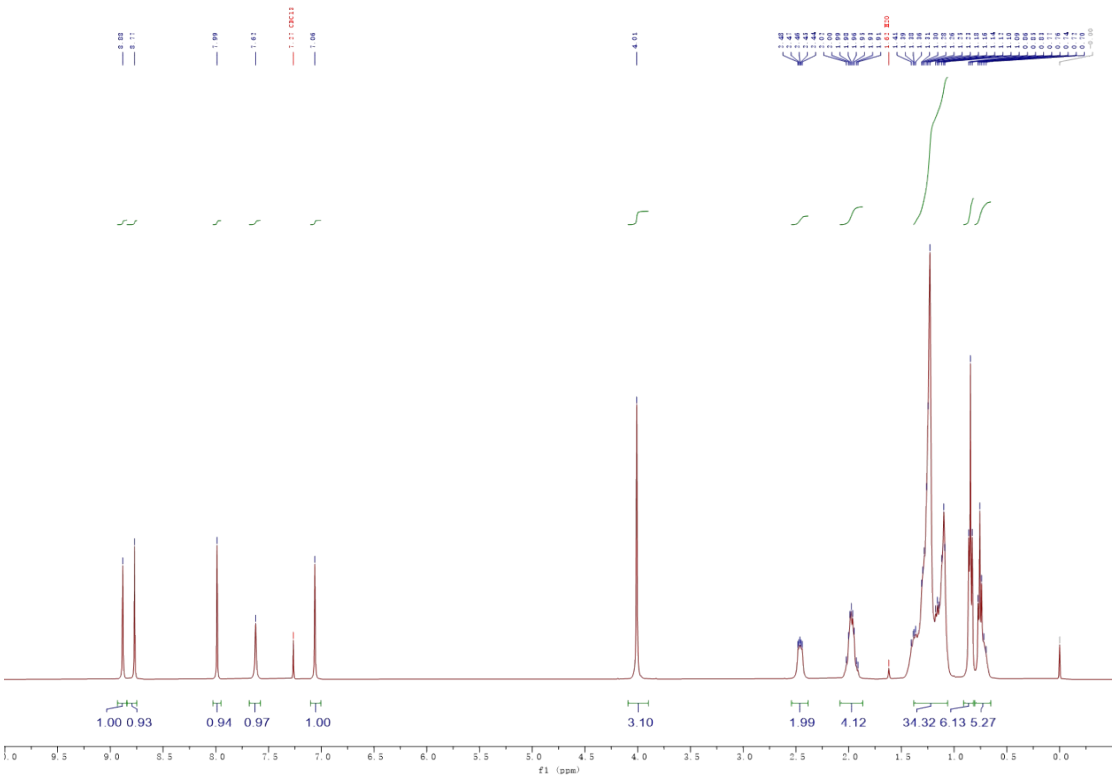


Figure S7. ^{1}H NMR (400 MHz) of compound **FOM-2**.

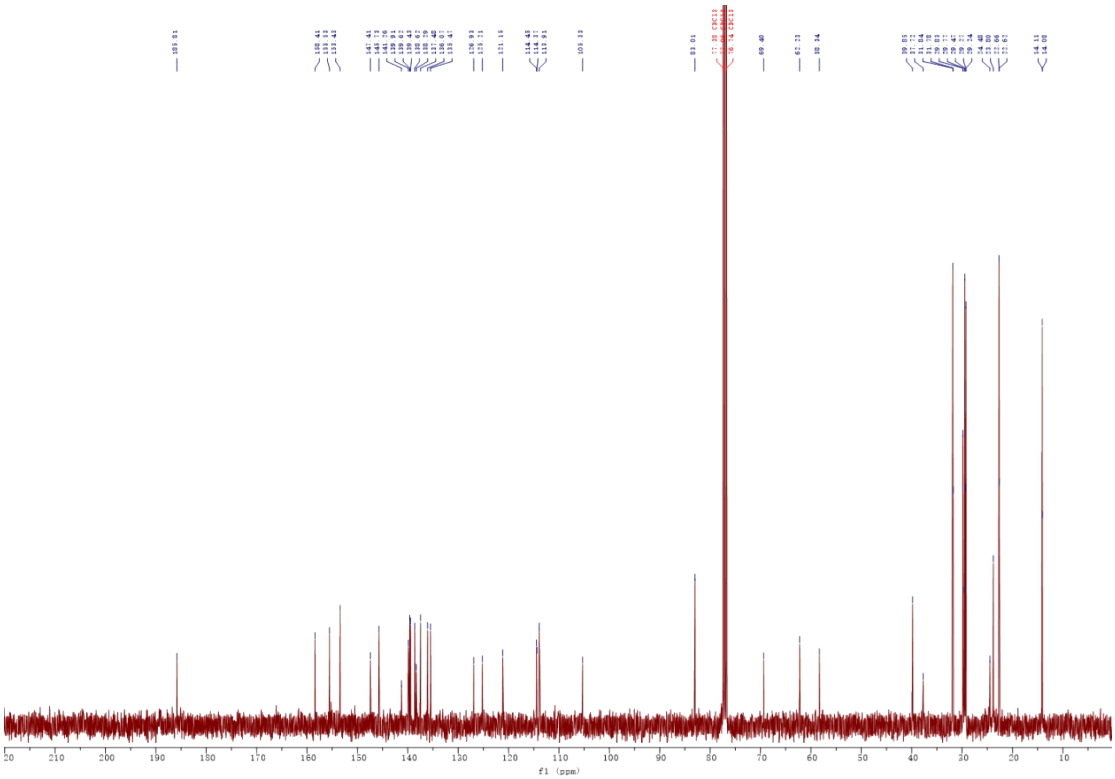


Figure S8. ^{13}C NMR (101 MHz) of compound **FOM-2**.

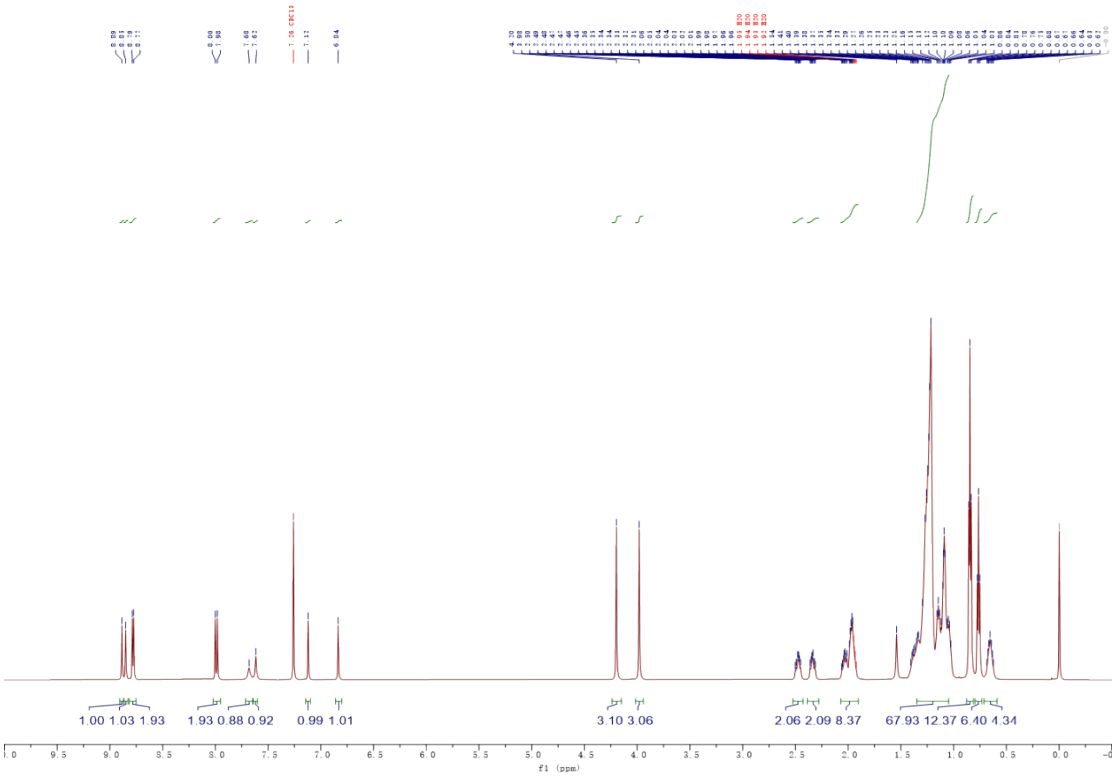


Figure S9. ^{1}H NMR (600 MHz) of compound **FOM-3**.

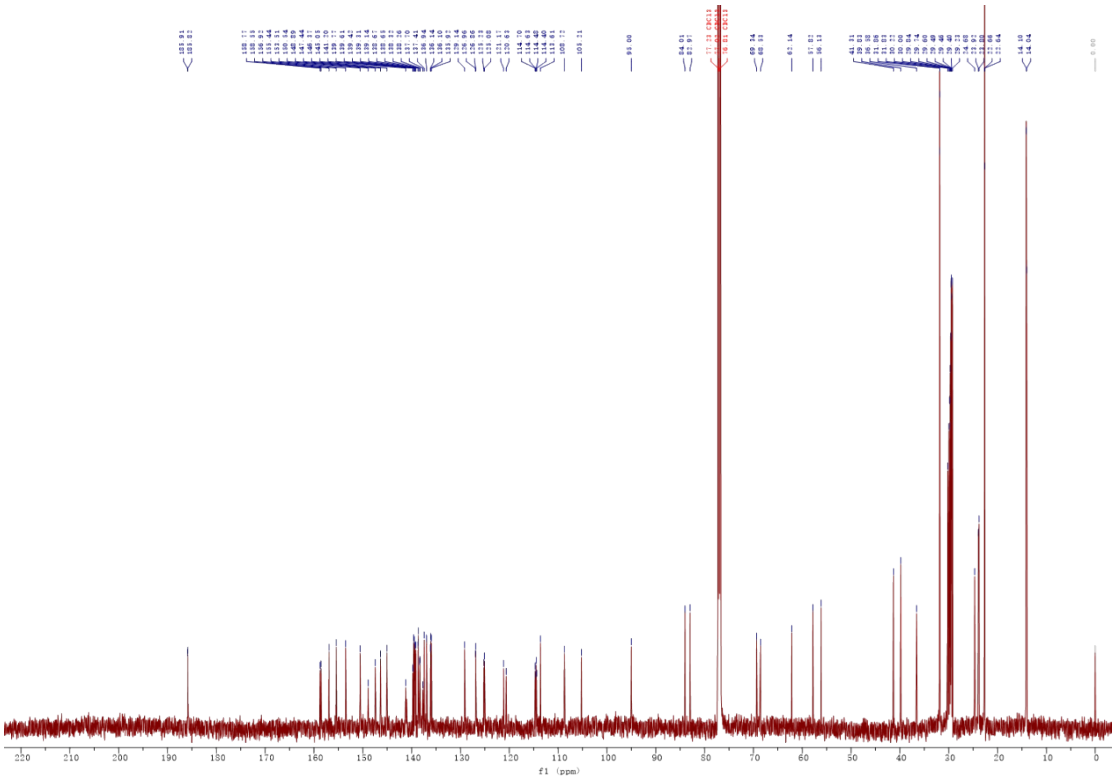


Figure S10. ^{13}C NMR (151 MHz) of compound **FOM-3**.

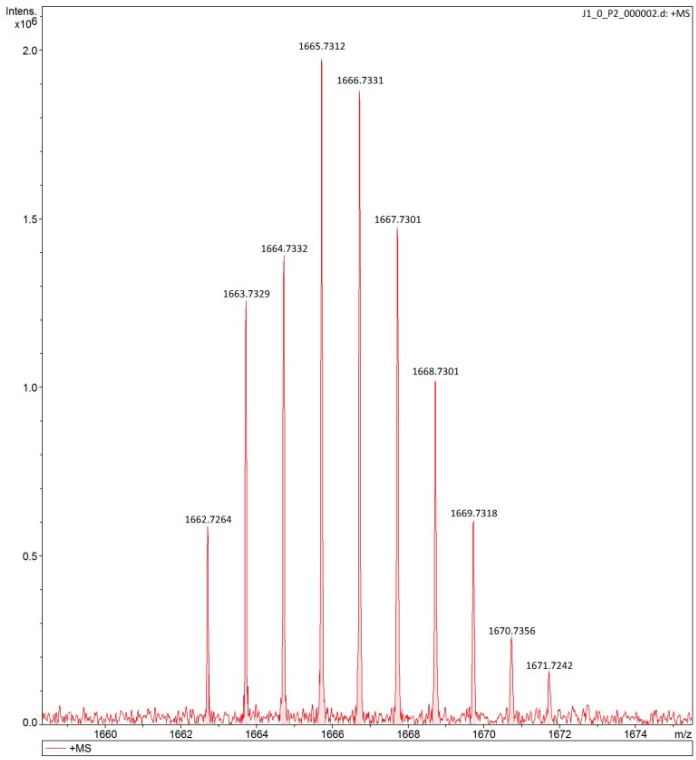


Figure S11. HR-MS spectrum of compound FOM-1.

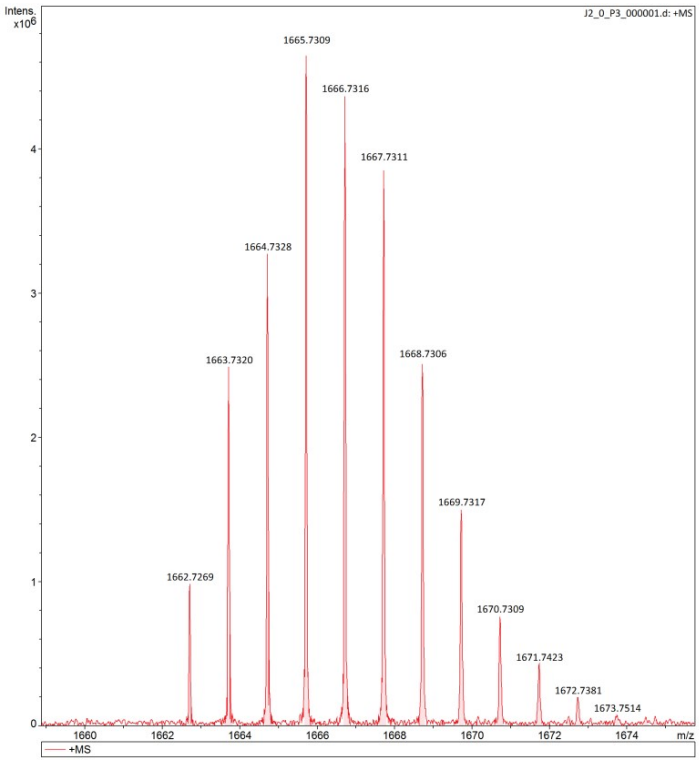


Figure S12. HR-MS spectrum of compound **FOM-2**.

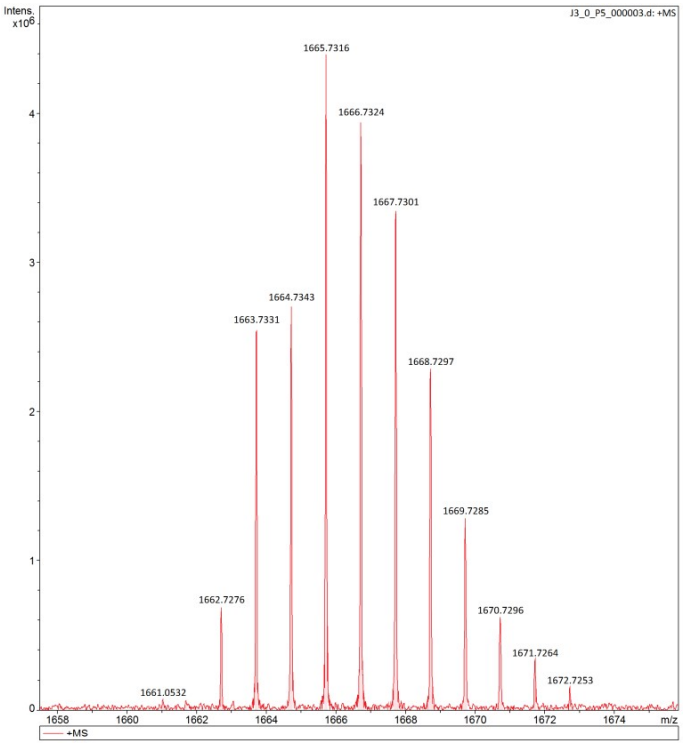


Figure S13. HR-MS spectrum of compound **FOM-3**.