

# Supporting Information for

## $\pi$ -Extended Chlorinated Non-fullerene Acceptors Achieving

### High Performance Organic Solar Cells

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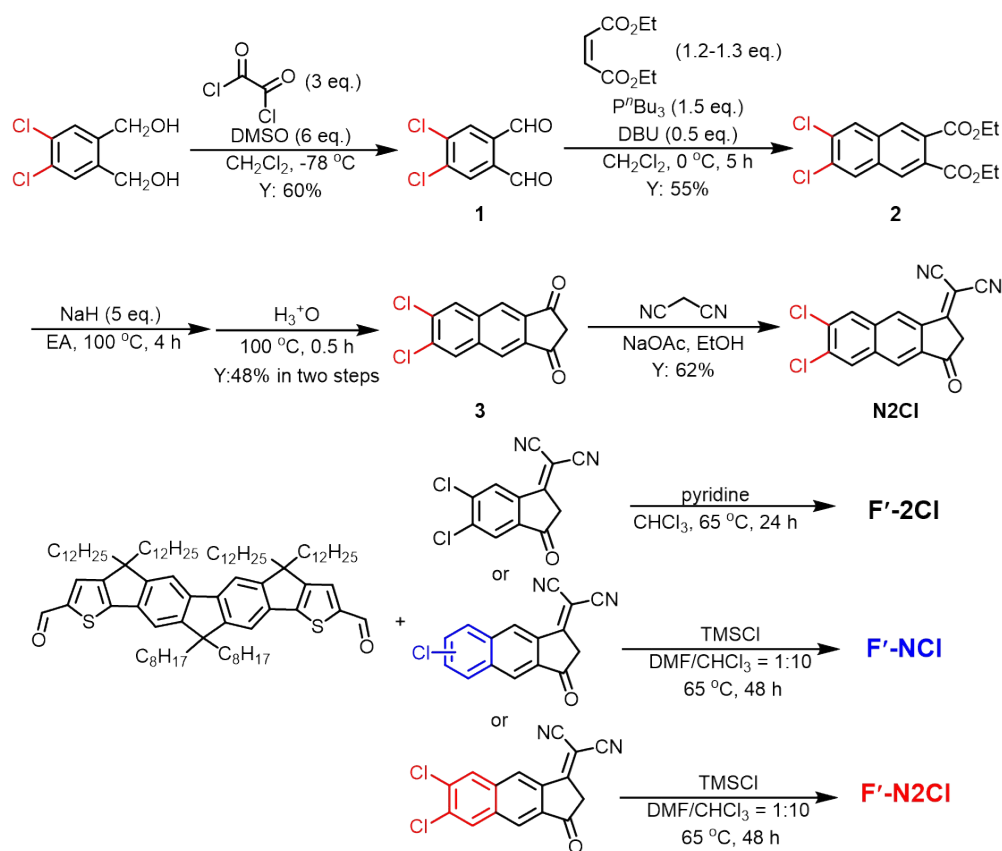
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## 1. Materials and synthesis.

All the starting materials were purchased from commercial suppliers and used without further purification unless indicated otherwise. Polymeric donor **PM6** end groups INCN-2Cl were purchased from Solarmer Material (Beijing) Inc, and end group NCl was purchased from Senior Material (Suzhou) Inc. NFAs **F'-2Cl**, **F'-NCl** and **F'-N2Cl** were synthesized based on our previously reported methods as follows. All reactions and manipulations were carried out under argon atmosphere with the use of standard Schlenk techniques.



**Scheme S1.** The detailed synthesis of end group **N2Cl** and NFAs **F'-2Cl**, **F'-NCl** and **F'-N2Cl**

### Synthesis of compound 4,5-Dichlorophthalaldehyde **1**

To a round bottom flask charged with a magnetic stir bar and an addition funnel was added oxalyl chloride (8.3 mL, 97 mmol, 2.2 eq.) and dichloromethane (100 mL). The reaction mixture was cooled to  $-78\text{ }^\circ\text{C}$  and a solution of dimethylsulfoxide (14 mL, 193 mmol, 4.4 eq.) in dichloromethane (28 mL) was added dropwise via the addition funnel. After 20 min, a solution of 4,5-dichloro-1,2-benzenedimethanol (9.1 g, 44.1

mmol, 1 eq.) in 1:1 DCM–DMSO (66 mL) was added dropwise. After 1 h, triethylamine (109 mL, 780 mmol, 18 eq.) was added slowly to the reaction mixture, which was subsequently warmed to room temperature over 1 h. The reaction mixture was diluted by addition of cold water (320 mL). The aqueous layer was separated and extracted with DCM (2 × 160 mL). The organic layers were combined, washed with saturated aqueous bicarbonate (160 mL) and brine (320 mL), dried over MgSO<sub>4</sub>, filtered and concentrated. The resulting residue was dissolved in THF (150 mL) and filtered to remove remaining ammonium salts. The product was purified by sublimation at 110 °C under vacuum, followed by recrystallizing twice from chloroform and drying overnight under vacuum. 4,5-Dichlorophthalaldehyde (**1**) was obtained as a light-yellow solid (5.3 g, 60%). The <sup>1</sup>H NMR and <sup>13</sup>C NMR are the same as the reference literature.<sup>[1]</sup>

#### *Synthesis of compound* diethyl 6,7-dichloronaphthalene-2,3-dicarboxylate **2**

The tributylphosphine (1.3-1.4 eq.) was added dropwise via syringe to a stirred CH<sub>2</sub>Cl<sub>2</sub> solution of diethyl maleate (1.2-1.3 eq., 2 mmol/mL) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 30 min. The Wittig reagent thus generated was added dropwise via syringe to a stirred CH<sub>2</sub>Cl<sub>2</sub> solution of **1** (1 eq. 5 mmol/mL) at 0 °C. After the completion of the addition, a CH<sub>2</sub>Cl<sub>2</sub> solution of DBU (0.1 eq., 5 mmol/mL) was added dropwise via syringe to the reaction mixture. The reaction mixture was stirred at room temperature for another 3 hours. Water was added to quench the reaction and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic layer was dried over anhydrous MgSO<sub>4</sub> and the volatiles were removed under reduced pressure. The resulting slurry was purified by column chromatography on silica gel (hexane-CH<sub>2</sub>Cl<sub>2</sub>, 1:1 and 1:3 to pure CH<sub>2</sub>Cl<sub>2</sub>). White solid, 55% isolated yield. The <sup>1</sup>H NMR and <sup>13</sup>C NMR are the same as the reference literature.<sup>[2]</sup>

#### *Synthesis of compound* 6,7-dichloro-1*H*-cyclopenta[b]naphthalene-1,3(2*H*)-dione **3**

According to the literature<sup>[3]</sup>, sodium hydride dispersed in mineral oil (60%, 0.50 g, 10.4 mmol) was placed in a two-neck flask under nitrogen. A solution of diethyl 6,7-dichloro-2,3-naphthalenedicarboxylate (0.5 g, 1.47 mmol) in ethyl acetate (2.5 mL) was slowly added, and the reaction mixture was heated under reflux for 4 h. After being cooled to room temperature, the solid was filtered off, washed with a mixture of ethanol/diethyl ether (1/1, 10 mL); it was then dispersed into a hot solution of hydrochloric acid (2%, 50 mL) and stirred for a few minutes during decarboxylation.

After being cooled to room temperature, the solid crude product was filtered off and purified by flash chromatography (hexane/ethyl acetate). Yield: 0.64 g (48%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.42 (s, 2H), 8.24 (s, 2H), 3.39 (s, 2H). The product is unstable and metamorphic in air or solvent, and should be used as soon as possible.

*Synthesis of molecule 2-(6,7-dichloro-3-oxo-2,3-dihydro-1H-cyclopenta[*b*]naphthalen-1-ylidene)malononitrile N2Cl*

A 15 mL oven dried round bottom flask was charged with **3** (1.06g, 3.4 mmol, 1.0 eq.), malononitrile (337 mg, 5.1 mmol, 1.5 eq.), sodium acetate (0.3 g, 5.1 mmol, 1.5 eq.), and ethanol (5 mL). After stirring for 72 h, 1M HCl (15 mL) was added and the mixture was stirred for 30 min, at which point the precipitate that formed was collected by vacuum filtration. The solids were then purified by column chromatography (SiO<sub>2</sub>:CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>OH), and yield **N2Cl** as a golden powder (510 mg, 62%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.23 (s, 1H), 8.07 (s, 1H), 8.03 (s, 1H), 7.67 (s, 1H), 3.35 (s, 1H); HRMS (ESI) calculated for [M-H, C<sub>16</sub>H<sub>6</sub>Cl<sub>2</sub>N<sub>2</sub>O]<sup>-</sup>: 310.9784, found 310.9780.

*Synthesis of compound F'-2Cl*

Under the protection of argon, compound **F'-CHO** (100 mg, 0.076 mmol) and 2-(5,6-dichloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (**INCN-2Cl**) (100 mg, 0.38 mmol) was dissolved in dry CF (50 mL), followed by the addition of pyridine (0.3 mL). After stirring at room temperature for 12 h, the mixture was concentrated in vacuum. MeOH (50 mL) was poured into the residues. The crude was precipitated and filtered through qualitative filter paper. Then the residue was dissolved in chloroform. The solvent was removed by reduced pressure and further purified by silica gel (eluant: PE/CF = 1:1.25) and then recrystallized from CF/hexane/CH<sub>3</sub>OH to give **F'-2Cl** as a dark blue solid (89 mg, 49.5%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.01 (s, 2H), 8.79 (s, 2H), 7.96 (s, 2H), 7.75 (s, 2H), 7.70 (s, 2H), 7.65 (s, 2H), 2.17 – 2.03 (m, 8H), 2.01 – 1.90 (m, 4H), 1.30 – 1.03 (m, 88H) 1.00 – 0.67 (m, 34H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 186.02, 163.52, 158.56, 157.20, 156.74, 152.55, 142.83, 140.58, 139.45, 139.30, 139.22, 138.91, 138.61, 136.57, 136.08, 126.90, 125.04, 120.25, 116.49, 114.68, 114.61, 114.48, 68.74, 54.76, 54.22, 40.35, 39.10, 31.87, 31.74, 29.99, 29.87, 29.69, 29.60, 29.55, 29.37, 29.30, 29.18, 29.16, 24.56, 23.90, 22.64, 22.57, 14.06, 14.03; HRMS (ESI) calculated for [M+H, C<sub>121</sub>H<sub>151</sub>Cl<sub>4</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>]<sup>+</sup>: 1798.9719, found 1798.9654.

*Synthesis of compound F'-NCl*

Under the protection of argon, compound **F'-CHO** (100 mg, 0.076 mmol) and end group **NCl** (170 mg, 0.61 mmol) was dissolved in dry CF and DMF (30 mL:3 mL), followed by the addition of TMSCl (1.0 mL). After stirring at room temperature for 48 h, the mixture was concentrated in vacuum. MeOH (50 mL) was poured into the residues. The crude was precipitated and filtered through qualitative filter paper. Then the residue was dissolved in chloroform. The solvent was removed by reduced pressure and further purified by silica gel (eluant: PE/CF = 1:1 – 1:1.5) and then recrystallized from CF/hexane/CH<sub>3</sub>OH to give **F'-NCl** as a dark blue solid (65 mg, 36%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.21 – 9.04 (m, 4H), 8.36 (s, 1H), 8.29 (s, 1H), 8.12 – 8.12 (m, 4H), 7.78 (s, 1H), 7.71 (s, 2H), 7.69 – 7.62 (m, 4H), 2.21 – 2.03 (m, 8H), 2.02 – 1.90 (m, 4H), 1.30 – 1.03 (m, 88H), 1.01 – 0.66 (m, 34H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 187.71, 163.39, 160.14, 157.20, 156.75, 152.54, 142.78, 141.10, 139.23, 139.18, 138.85, 136.74, 136.69, 136.00, 135.90, 135.79, 135.64, 135.00, 134.29, 133.92, 133.47, 133.23, 131.90, 131.41, 130.55, 130.32, 129.20, 128.76, 126.46, 125.48, 123.99, 123.08, 122.78, 122.74, 116.48, 115.32, 114.66, 67.21, 66.87, 54.72, 54.22, 40.37, 39.14, 31.86, 31.75, 30.02, 29.91, 29.61, 29.59, 29.56, 29.39, 29.30, 29.27, 29.21, 29.18, 24.58, 23.94, 22.63, 22.58, 14.06; HRMS (ESI) calculated for [M+H, C<sub>121</sub>H<sub>153</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>]<sup>+</sup>: 1830.6005, found 1830.0816.

#### *Synthesis of compound F'-N2Cl*

Under the protection of argon, compound **F'-CHO** (80 mg, 0.061 mmol) and end group **N2Cl** (0.2 g, 0.61 mmol) was dissolved in dry CF and DMF (30 mL:3 mL), followed by the addition of TMSCl (1.0 mL). After stirring at room temperature for 48 h, the mixture was concentrated in vacuum. MeOH (50 mL) was poured into the residues. The crude was precipitated and filtered through qualitative filter paper. Then the residue was dissolved in chloroform. The solvent was removed by reduced pressure and further purified by silica gel (eluant: PE/CF = 1:1 – 1:1.5) and then recrystallized from CF/hexane/CH<sub>3</sub>OH to give **F'-N2Cl** as a dark blue solid (108 mg, 93%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.10 (s, 4H), 8.28 (s, 2H), 8.22 (s, 2H), 8.19 (s, 2H), 7.79 (s, 2H), 7.72 (s, 2H), 7.67 (s, 2H), 2.19 – 2.04 (m, 8H), 2.04 – 1.90 (m, 4H), 1.32 – 1.05 (m, 88H), 1.00 – 0.65 (m, 34H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 187.03, 164.18, 159.27, 157.37, 156.94, 152.65, 142.98, 141.21, 139.21, 136.68, 135.58, 134.59, 134.56, 134.23, 133.75, 130.96, 130.52, 125.02, 122.62, 122.14, 116.66, 115.17, 115.10, 114.73, 67.10, 54.77, 54.23, 40.42, 39.13, 31.84, 31.75, 30.04, 29.94, 29.65, 29.62, 29.59, 29.55, 29.40, 29.29, 29.23, 29.19, 24.63, 23.99, 22.61, 22.57, 14.04. HRMS

(ESI) calculated for  $[M+H, C_{121}H_{151}Cl_4N_4O_2S_2]^+$ : 1899.0032, found 1899.0018.

## 2. Fabrication of OSC devices

The OSCs devices were fabricated with the structure of ITO/ZnO/PFN-Br/ Active layer /MoO<sub>x</sub>/Ag. The ITO-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 minutes each time and subsequently dried by a nitrogen flow. A 30 nm thick layer of ZnO precursor solution was spin-coated (3000 rpm, 20 s) onto the ITO surface. After baked at 200 °C for 1 h, the substrates were transferred into an argon-filled glove box. A thin film of PFN-Br was spin-coated on ZnO layer (5000 rpm, 13 s). Subsequently, the active layer was spin-coated from blend chlorobenzene. Solvents, the concentration of donor, different D:A ratio under different post treatments, and different kinds of additives and dosage are carefully determined. The optimal condition is D/A ratio 1:1, 0.3% DIO in chlorobenzene, in high vacuum for 30 min. After post treatment, MoO<sub>x</sub> (~6 nm) and Ag (~70 nm) was successively evaporated onto the active layer through a shadow mask.

## 3. Measurements and Characterizations

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were taken on a Bruker AV400 Spectrometer. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry were performed on a Bruker Auto flex III instrument. Varian 7.0T FTMS was used to achieve the HRMS data. UV-vis spectra were obtained with a Cary 5000 Spectrophotometers. Cyclic voltammogram (CV) was performed with a LK2010 Microcomputer based Electrochemical Analyzer at a scan rate of 100 mV/s. Thermogravimetric analyses (TGA) were carried out on a NETZSCH STA 449 F5 Jupiter instrument under a purified nitrogen gas. The heating rate is a 10 °C/ min heating rate. The current density-voltage (*J-V*) curves of photovoltaic devices were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under simulated illumination of 100 mW cm<sup>-2</sup> with AM 1.5 G irradiation using a xenon-lamp-based solar simulator [Oriel 96000] in an argon-filled glove box. EQEs of the encapsulated

devices were obtained with a halogen-tungsten lamp, monochromator, optical chopper, and lock-in amplifier in air and the photon flux was determined by a calibrated silicon photodiode. Atomic force microscopy (AFM) images were performed using in tapping mode on a Bruker Multi Mode 8 atomic force microscope. Transmission electron microscopy (TEM) was performed on a Philips Technical G2 F20 at 200 kV. The GIWAXS (grazing incidence wide angle X-ray scattering) samples were prepared on ZnO-coated Si substrates using the same preparation conditions as for devices and All samples were deposited on the silicon and were irradiated at a fixed X-ray incident angle of  $0.2^\circ$  with an exposure time of 9 h. The hole and electron mobility were measured using the space charge limited current (SCLC) method, employing a diode configuration of glass/ITO/PEDOT:PSS/active layer/Au for hole and glass/ITO/ZnO/active layer/Al for electron by taking the dark current density in the range of 0-8 V and fitting the results to a space charge limited form, where SCLC is described by:

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

where  $J$  is the current density,  $L$  is the film thickness of the active layer,  $\mu$  is the hole or electron mobility,  $\varepsilon_r$  is the relative dielectric constant of transport medium,  $\varepsilon_0$  is the permittivity of free space ( $8.85 \times 10^{-12}$  F m<sup>-1</sup>),  $V$  ( $= V_{\text{appl}} - V_{\text{bi}}$ ) is the internal voltage in the device, where  $V_{\text{appl}}$  is the applied voltage to the device and  $V_{\text{bi}}$  is the built-in voltage due to the relative work function difference of the two electrodes. The hole and electron mobility of the solar cell blend are deduced from the intercept value of  $9\varepsilon_0\varepsilon_r\mu/(8L^3)$  by linearly plotting  $\ln(J)$  vs.  $\ln(V)$  (the slope of  $\ln(J)$  vs.  $\ln(V)$  is  $\approx 2$ ).

The current density-voltage ( $J$ - $V$ ) characteristics of photovoltaic devices were obtained using a Keithley 2400 source-measure unit. The photocurrent was measured under illumination simulated 100 mW cm<sup>-2</sup> AM1.5G irradiation using SAN-EI XES-70S1 solar simulator, calibrated with a standard Si solar cell. The EQE spectrum was measured using a QE-R Solar Cell Spectral Response Measurement System (Enli Technology Co., Ltd., Taiwan).

For the transient photocurrent (TPC) and transient photovoltage (TPV) measurements,

the device was mounted on a conductive clip and under steady-state illumination from focused Quartz Tungsten-Halogen Lamp light source. The measurements were performed with background response similar to open-circuit voltage. An optical perturbation is applied to the device with a 1 kHz femtosecond pulse laser under 450 nm excitation. The TPV signal was acquired by a digital oscilloscope at open-circuit condition. TPC signal was measured under approximately short-circuit condition by applying a 50  $\Omega$  resistor. The photovoltage decay kinetics of all devices follow a mono-exponential decay:  $\delta V = A \exp(-t/\tau)$ , where  $t$  is the time and  $\tau$  is the charge carrier lifetime.

Electroluminescence (EL) and photoluminescence (PL) spectra were taken using a Kymera-328I spectrograph and an EMCCD purchased from Andor Technology (DU970P). Injection current used for EL was 1 mA cm<sup>-2</sup>, and excitation wavelength used for the PL measurements was 650 nm. EQE<sub>EL</sub> measurements were done from 0.01 V to 2.5 V using a home built setup using a Keithley 2400 to inject current to the solar cells. Emission photon-flux from the solar cells was recorded using a Si detector (Hamamatsu s1337-1010BQ) and a Keithley 6482 picoammeter. FTPS-EQE measurements were done from 500 nm to 1300 nm using a halogen lamp light source, chopped at a frequency of 173 Hz, a monochromator (Newport CS260), a Stanford SR830 lock-in amplifier, a Stanford SR570 current amplifier, and a set of long pass filters. Lamp intensity was calibrated using a Si detector (Hamamatsu s1337-1010BQ).

### **The calculation of $\Delta E_1$ , $\Delta E_2$ and $\Delta E_3$**

The detailed components of  $E_{loss}$  can be categorized into two parts based on the SQ limit, as shown in the following Equation:<sup>[4]</sup>

$$E_{loss} = (E_{gap} - qV_{OC}^{SQ}) + (qV_{OC}^{SQ} - qV_{OC}^{rad}) + (qV_{OC}^{rad} - qV_{OC})$$

inhere,



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

Where  $\phi_{BB}(E)$  is black body emission at room temperature, thus, for the unavoidable radiative recombination  $\Delta E_1$

$$\Delta E_1 = E_{gap} - qV_{OC}^{SQ}$$

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

Thus, for the unavoidable radiative recombination  $\Delta E_2$

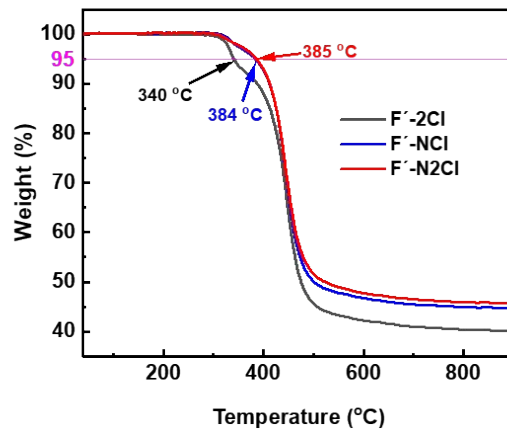
$$\Delta E_2 = qV_{OC}^{SQ} - qV_{OC}^{rad}$$

Finally, for the non-radiative recombination loss  $\Delta E_3$

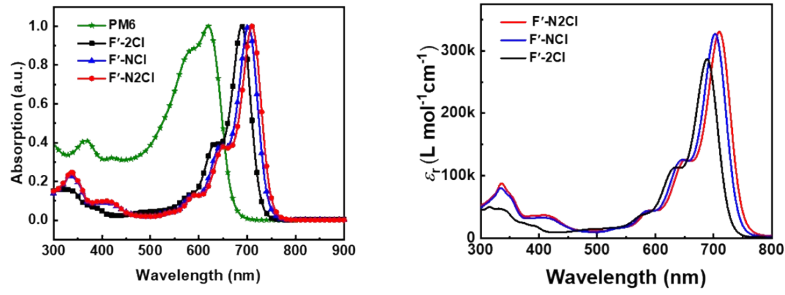
$$\Delta E_3 = qV_{OC}^{rad} - qV_{OC}$$

Where  $V_{oc}$  is the open circuit voltage of the PSC.

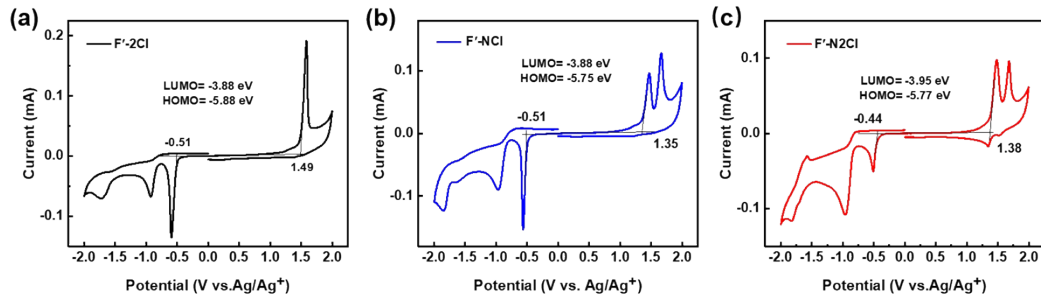
#### 4. Supplementary Figures and Tables



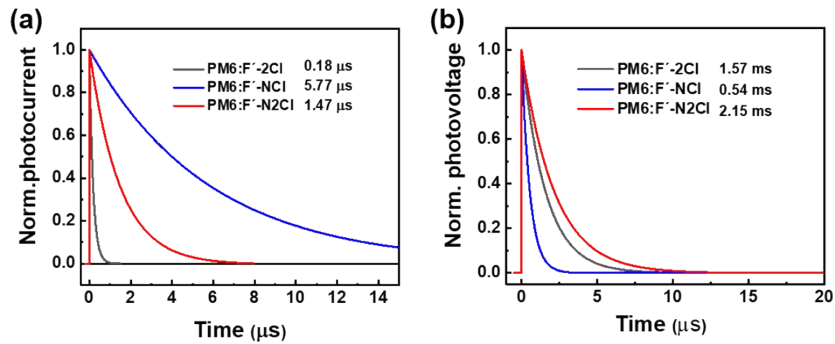
**Fig. S1** Thermogravimetric analysis (TGA) curve of F'-2Cl, F'-NCl and F'-N2Cl with a heating rate of 10 °C/min under N<sub>2</sub> atmosphere.



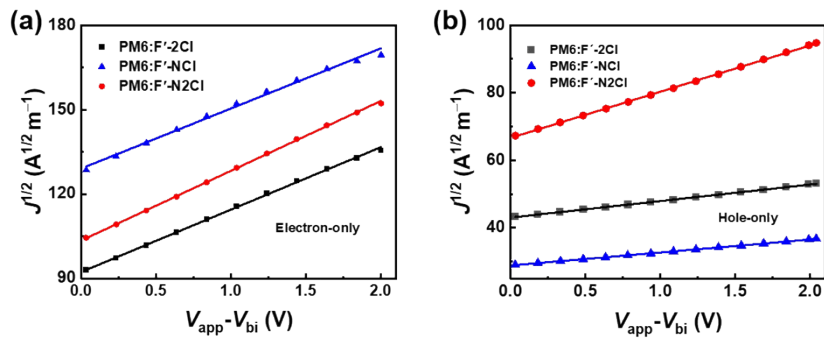
**Fig. S2** The normalized absorption spectra of PM6, F'-2Cl, F'-NCl and F'-N2Cl, the molar absorption coefficient in diluted CF solution.



**Fig. S3** The cyclic voltammetry (CV) measurements of F'-2Cl (a), F'-NCl (b) and F'-2Cl (c) in solid films. The corresponding potential values are extracted by the crossing points of the two tangent lines. The energy levels are estimated from the oxidation and reduction wave in CV spectra, and the measurement was referenced by the energy level of Fc/Fc<sup>+</sup> (-4.8 eV below vacuum).



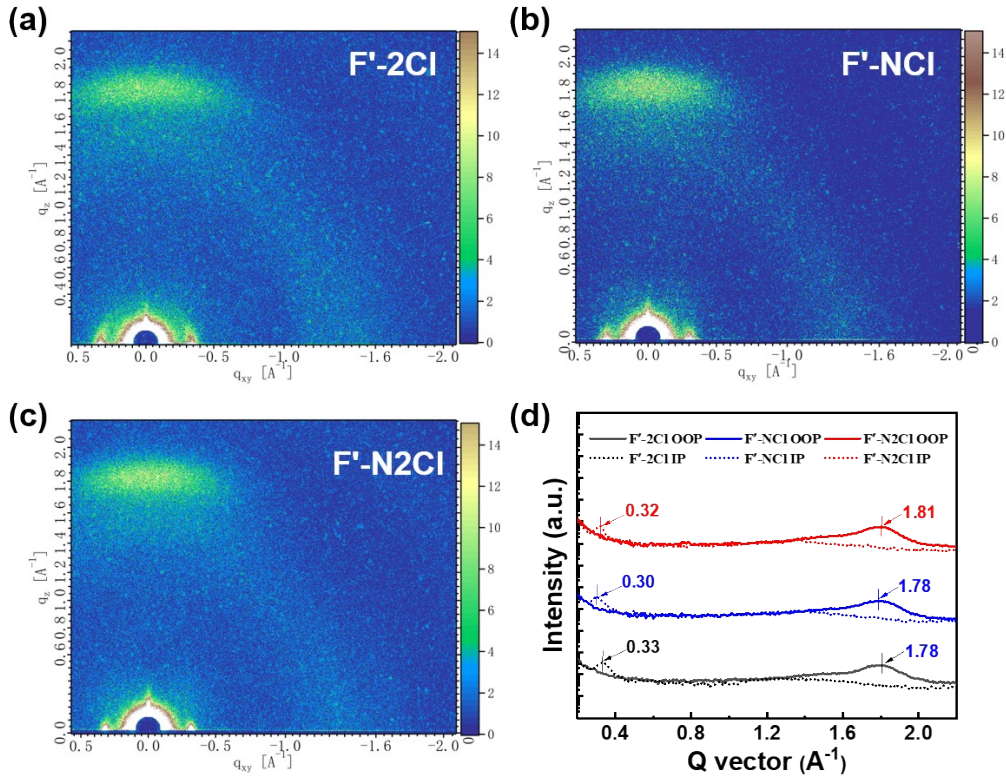
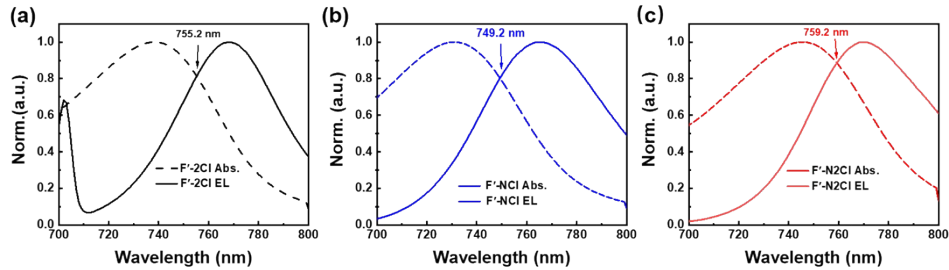
**Fig. S4** (a) Transient photocurrent (TPC) measurements curves and (b) transient photovoltage (TPV) measurements curves.



**Fig. S5** The current-density-voltage ( $J$ - $V$ ) plots for (a) electron-only and (b) hole-only based on **PM6:F'-2Cl**, **PM6:F'-NCl** and **PM6:F'-N2Cl** devices.

**Table S1** The mobilities of three active layers obtained by SCLC measurement

Active layers	$L$ (nm)	$\mu_h$ ( $\times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )	$\mu_e$ ( $\times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )
PM6:F'-2Cl	128	1.68	3.45
PM6:F'-NCl	125	0.96	2.98
PM6:F'-N2Cl	118	10.13	3.38

**Fig. S6.** 2D GIWAXS pattern for neat films F'-2Cl (a), F'-NCl (b) and F'-N2Cl (c); and corresponding 1D GIWAXS image of pristine films in-plane and out-of-plane directions (d).**Fig. S7** The energy gap of PM6:F'-2Cl (a); PM6:F'-NCl (b) and PM6:F'-N2Cl (c) estimated from the intersection of the normalized optical absorption and EL curves.

**Table S2** Photovoltaic performance of devices based on **PM6:F'-N2Cl** with D/A = 1:1 in different solvents.

Solvents	Post treatments	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
chlorobenzene	vacuum 30 min	0.934	19.75	74.98	13.77
	TA 80 °C, 10 min	0.914	19.77	75.48	13.57
	TA 100 °C 5 min	0.895	20.50	73.58	13.43
chloroform	vacuum 30 min	0.911	18.71	46.61	7.91
	TA 80 °C, 10 min	0.894	18.68	44.88	7.49
	TA 100 °C 5 min	0.872	18.55	44.18	7.12

**Table S3** Photovoltaic performance of the solar cells based on **PM6:F'-N2Cl** blend films with different D:A ratio under different post treatments in chlorobenzene.

D:A	Post treatments	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
1:0.8	As cast	0.935	19.22	74.14	13.26
	80 °C 10 min	0.914	19.70	74.11	13.29
	100 °C 10 min	0.907	19.57	74.46	13.15
1:1	As cast	0.934	19.75	74.98	13.77
	80 °C 10 min	0.914	19.77	75.48	13.57
	100 °C 10 min	0.895	20.50	73.58	13.43
1:1.2	As cast	0.926	19.69	74.44	13.51
	80 °C 10 min	0.905	19.85	74.88	13.38
	100 °C 10 min	0.897	19.70	75.36	13.26

**Table S4** Photovoltaic performance of devices based on **PM6:F'-N2Cl** = 1:1 with different kinds of additives and dosage in chlorobenzene.

Additive	Post treatments	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
none	vacuum 30 min	0.934	19.75	74.98	13.77
0.3% DIO	vacuum 30 min	0.927	20.31	74.68	14.13
	TA 100 °C 10min	0.902	20.40	72.93	13.48
0.5% DIO	vacuum 30min	0.932	18.74	72.74	12.68
	TA 100 °C 10min	0.907	18.96	72.04	12.37
0.7% DIO	vacuum 30min	0.920	18.91	73.16	12.31
	TA 100 °C 10min	0.886	16.46	69.47	10.14
0.3% CN	vacuum 30min	0.935	18.17	70.81	12.05
	TA 100 °C 10min	0.900	18.37	71.02	11.76
0.5% CN	vacuum 30min	0.926	18.73	71.21	12.37
	TA 100 °C 10min	0.893	18.46	68.54	11.32
0.7% CN	vacuum 30min	0.923	18.71	72.62	12.57
	TA 100 °C 10min	0.897	18.34	67.64	11.15

**Table S5** Photovoltaic performance of the solar cells based on **PM6:F'-NCl** = 1:1 and **PM6:F'-2Cl** = 1:1 blend films with different post treatments in chlorobenzene.

Active layer	Post treatment	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
<b>PM6:F'-2Cl</b>	vacuum 30 min	0.932	19.58	74.55	13.65
	80 °C 10 min	0.914	19.63	73.70	13.27
	100 °C 10 min	0.908	19.66	74.23	13.30
<b>PM6:F'-NCl</b>	vacuum 30 min	0.964	18.29	71.35	12.58
	80 °C 10 min	0.941	18.54	70.98	12.38
	100 °C 10 min	0.925	18.88	70.21	12.26

## 5. NMR spectra of New Compounds.

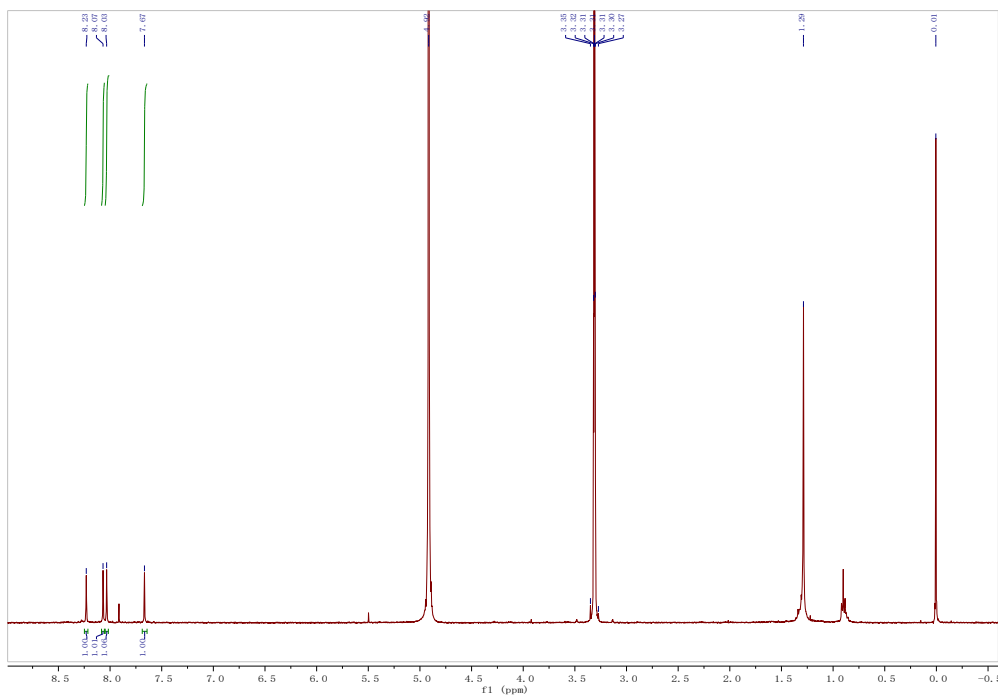


Fig. S8 <sup>1</sup>H NMR of compound N2Cl

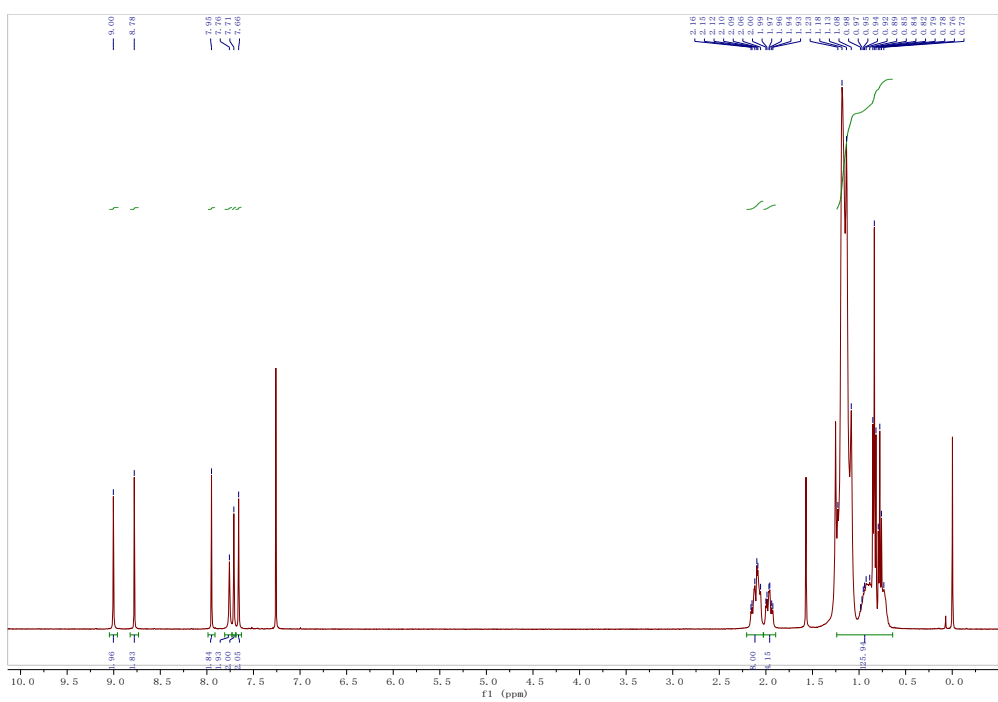


Fig. S9 <sup>1</sup>H NMR of compound F'-2Cl





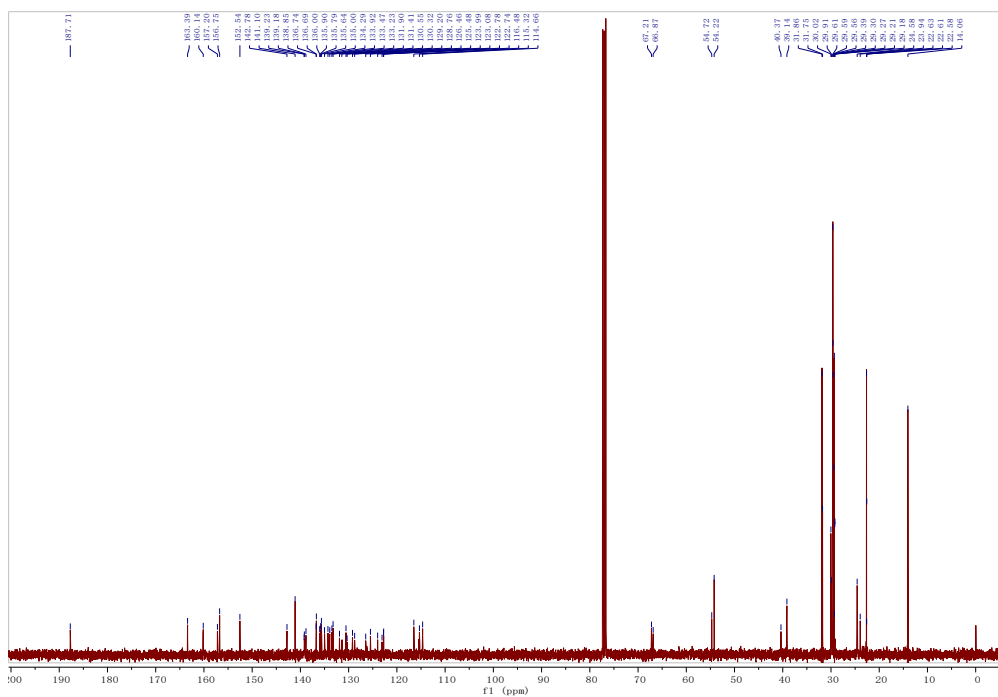


Fig. S12  $^{13}\text{C}$  NMR of compound F'-NCl

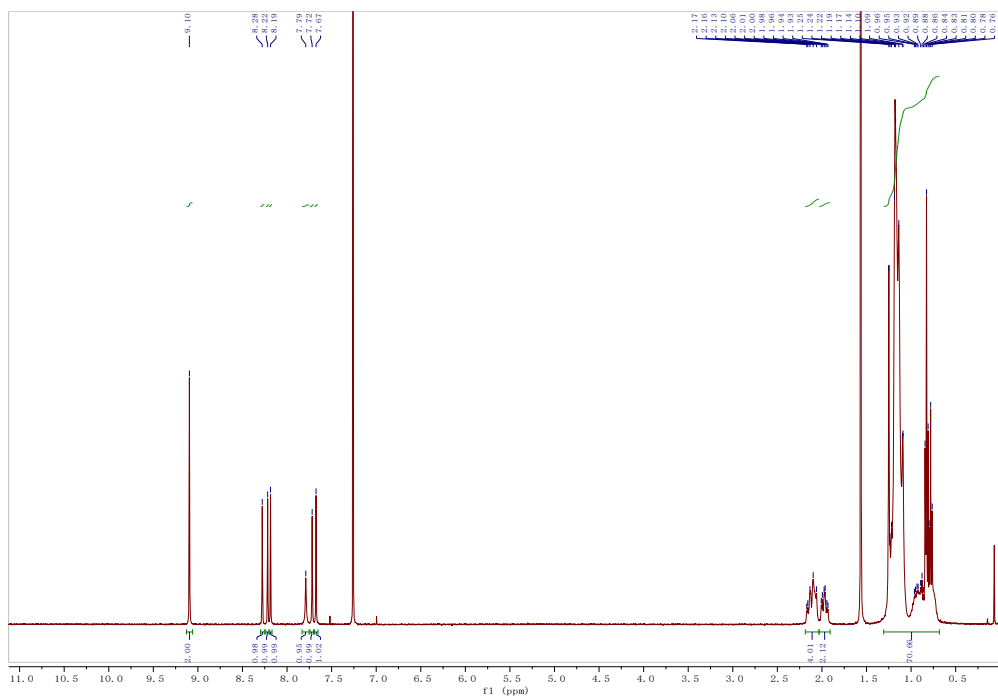
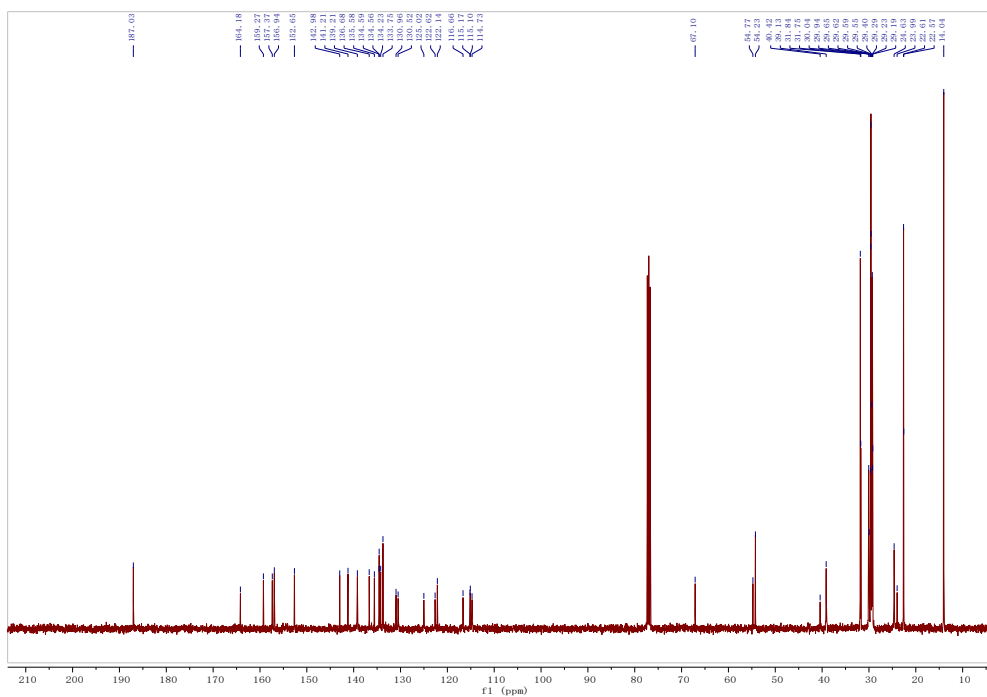
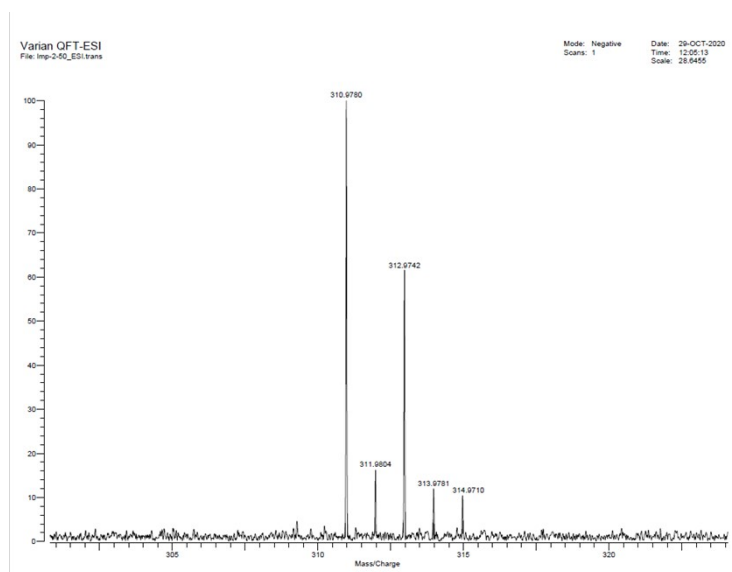


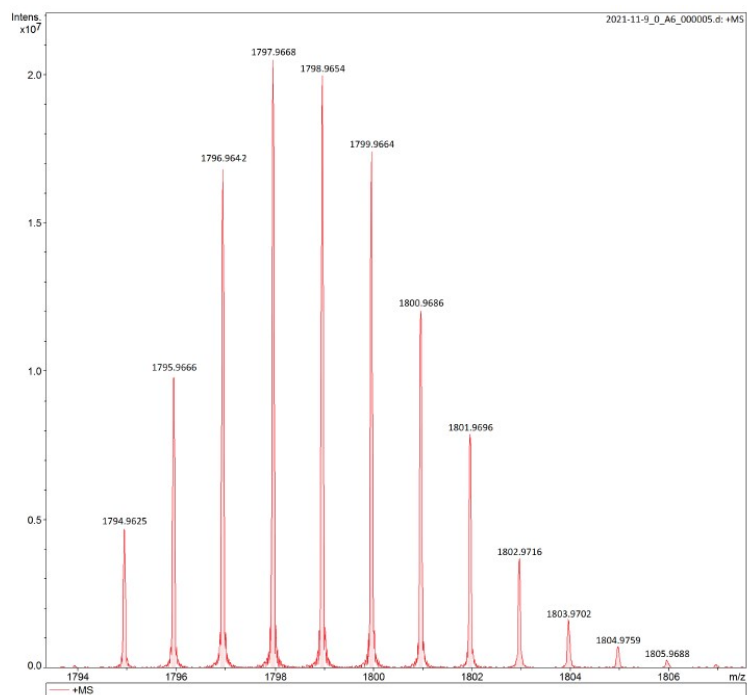
Fig. S13  $^1\text{H}$  NMR of compound F'-N2Cl



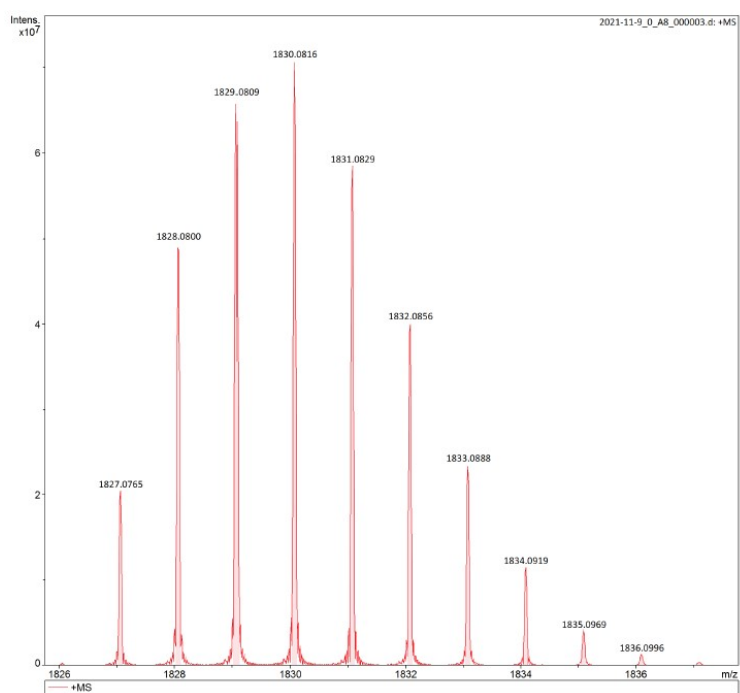
**Fig. S14**  $^{13}\text{C}$  NMR of compound F'-N2Cl



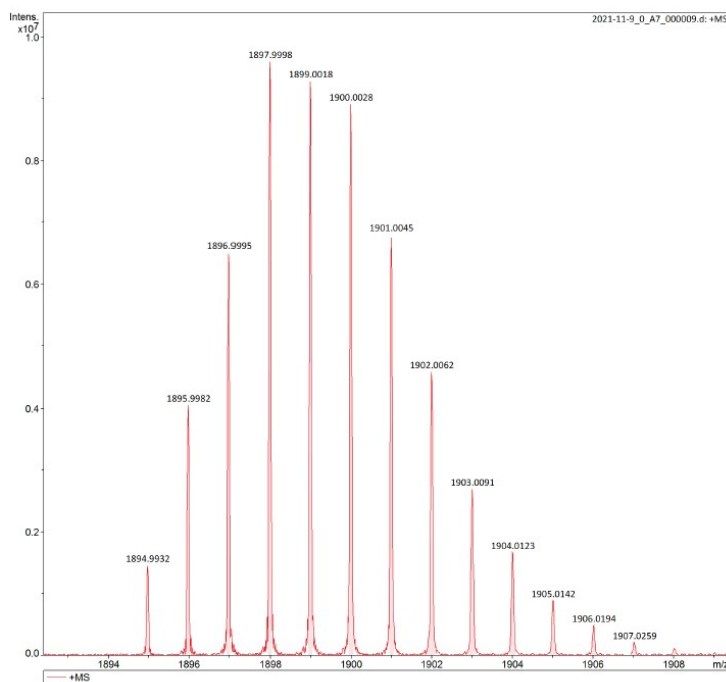
**Fig. S15** The ESI plot of compound N2Cl



**Fig. S16** MALDI-TOF spectrum of compound **F'-2Cl**



**Fig. S17** The MALDI-TOF plot of compound **F'-NCI**



**Fig. S18** The MALDI-TOF plot of compound **F'-N<sub>2</sub>Cl**

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