

Supplementary Information

Tuning Photophysical Properties of Acceptor–Donor–Acceptor Di-2-(2-oxindolin-3-ylidene) Malononitrile Materials via Extended π -Conjugation: A Joint Experimental and Theoretical Study

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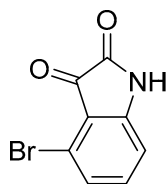
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1. General procedures and experimental details

Chemical reagents were purchased from Aldrich, Alfa Aesar and used as received. Reactions with air-sensitive materials were carried out under an argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230–240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminum-coated Merck Kieselgel 60 F254 plates. Known compounds, **13**, **14**, **15**, **16**, **17a**, **c**, were synthesized following the protocol reported in the literature and they gave identical spectroscopic data to those previously described in reference. Otherwise, all new compounds gave satisfactory spectroscopic data, ¹H NMR, ¹³C NMR spectroscopy and high-resolution mass spectrometry in accordance to their proposed structures. ¹H-NMR and ¹³C-NMR spectra were collected on a Bruker ARX 300 NMR spectrometer with deuterated solvents and tetramethylsilane (δ = 0 ppm) as the internal standard. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in parts per million (ppm). Multiplicities are denoted as: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad singlet. Mass spectrometry was performed by the "Fédération de Recherche" ICOA/CBM (FR2708) platform of Orléans in France. High-resolution ESI mass spectra (HRMS) were performed on a Bruker maXis Q-TOF in the positive ion mode. The analytes were dissolved in a suitable solvent at a concentration of 1 mg/mL and diluted 500 times in methanol (\approx 2 ng/mL). The diluted solutions (0.2 μ L) were delivered to the ESI source by a Dionex Ultimate 3000 RSLC chain used in FIA (Flow Injection Analysis) mode at a flow rate of 200 μ L/min with a mixture of CH₃CN/H₂O+0.1% of HCO₂H (65/35). ESI conditions were as follows: capillary voltage was set at 4.5 kV; dry nitrogen was used as nebulizing gas at 0.6 bar and as drying gas set at 200°C and 7.0 L/min. ESI-MS spectra were recorded at 1 Hz in the range of 50-3000 m/z. Calibration was performed with ESI-TOF Tuning mix from Agilent and corrected using lock masses at m/z 299.294457 (methyl stearate) and 1221.990638 (HP-1221). Data were processed using Bruker Data Analysis 4.4 software. UV-vis spectra were recorded on a Varian Cary model 500 UV-Vis-NIR spectrophotometer using standard quartz cells of 1 cm width and solvents of spectroscopic grade. Electrochemical measurements were carried out in dichloromethane solution with tetrabutylammonium perchlorate using a Metrohm Autolab PGSTAT12 Potentiostat. A three-electrode system was used with glassy carbon as a working electrode, a Pt wire as the counter electrode and reference electrode of saturated Ag/AgCl.

2. Synthetic procedures and characterization

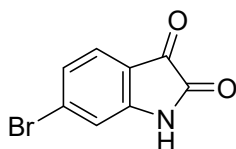
4-bromoindoline-2,3-dione (**13**):



13 was synthesized following a two-step protocol published in reference (1). Step one: synthesis of isonitrosoacetanilide. Chloral hydrate (4.5 g, 27 mmol, 1.12 eq) and Na₂SO₄ (12 g, 84 mmol, 3.5 eq) were dissolved in water (60 ml) in a 250 ml three-neck flask and warmed to 35 °C. A warm solution of the **11** (4.2 g, 24 mmol) in 20 ml of water, and an aqueous solution of concentrated HCl (2.6 ml) was added, a white precipitate of the amine sulfate was formed, followed by a warm solution of hydroxylamine hydrochloride (5.5g, 79 mmol, 3.3 eq) in 25 ml water. The mixture was stirred and heated at 80 °C for 2 h and then allowed to cool to room temperature. Filtered the yellow cream product and washed it with water. Dry overnight afforded the intermediate **12**. The crude product was directly used in the next step without further purification. Step two: synthesis of 4-bromoindoline-2,3-dione. Conc sulfuric acid (50 ml) was heated in a 100 ml flask at 60 °C. The dry isonitrosoacetanilide was added in small portion with stirring over 30 mins so that the temperature did not exceed 70 °C. The mixture was then heated to 80 °C for 10 mins, allowed to cool to room temperature. The reaction mixture is cooled on ice and left to stand overnight. The orange-red precipitate was filtered off and washed with water. The crude product was a mixture of **13** and **14**. The mixture was dissolved in a solution of NaOH (0.7 g) in 7.0 ml of water at 60 °C and then acidified with AcOH (3.0 ml). Then, the reaction mixture was standed for 1 h and cooled to room temperature. The precipitate was collected by filtration and washed with water to afford desired products **13** as an orange powder (43% yield over two steps).

¹H NMR (DMSO-d₆, 300 MHz, ppm) δ 11.19 (br, 1H, N-H), 7.46 (t, *J* = 8.0 Hz, 1H, Ar-H), 7.23 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.89 (d, *J* = 7.8 Hz, 1H, Ar-H).

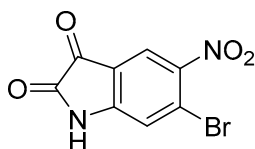
6-bromoindoline-2,3-dione (**14**):



14 was synthesized following a two-step protocol published in reference (1). Step one: synthesis of isonitrosoacetanilide. Conc H₂SO₄ (50 ml) was heated in a 100 ml flask at 60 °C. The dry isonitrosoacetanilide was added in small portion with stirring over 30 mins so that temperature did not exceed 70 °C. The mixture was then heated to 80 °C for 10 mins, then cooled to room temperature. The reaction mixture was cooled on ice and left to stand overnight. The orange-red precipitate was filtered off and washed with water. The crude product was a mixture of 4-bromoindoline and 6-bromoindoline. Then the mixture was dissolved in a solution of NaOH (0.7 g) in 7.0 ml of water at 60 °C and then acidified with acetic acid (3.0 ml). The solution was standed for 1 h to allow precipitation of solid. The resulting solid was filtered and the combined filtrate was acidified with concentrated HCl solution (6.0 mL) and standed for 2 h, then the precipitate was filtered off and washed with water. The obtained solid was dried overnight under vacuum to afford the desired product **14** as an orange-red powder (35% yield over two steps).

¹H NMR (300 MHz, DMSO-*d*₆) δ 11.14 (br, 1H, N---H), 7.41 (dd, *J* = 7.9, 2.5 Hz, 1H, Ar-H), 7.24 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.06 (s, 1H, Ar-H).

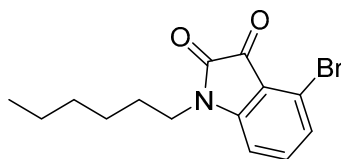
6-bromo-5-nitroindoline-2,3-dione (15):



15 was synthesized using the protocol published in reference (1). To a solution of NaNO₃ (188 mg, 2.21 mmol) in concentrated H₂SO₄ (4 mL) was added dropwise a solution of **14** (499 mg, 2.21 mmol) in concentrated H₂SO₄ (3 mL) at 0 °C. After 2h, the mixture was cooled, the reaction mixture was then poured into ice water (50 mL), and the precipitate was collected by filtration and washed with water three times to afford **15** as a yellow solid (598 mg, 82%).

¹H NMR (300 MHz, DMSO-*d*₆) δ 11.57 (br, 1H, N-H), 8.15 (s, 1H, Ar-H), 7.29 (s, 1H, Ar-H).

4-bromo-1-hexylindoline-2,3-dione (16):



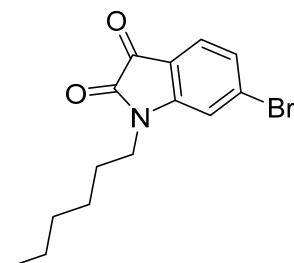
16 was synthesized using the protocol published in reference (1). In an oven-dried three-necked, round-bottomed flask equipped with a magnetic stir bar, compound **13** (1.0 g, 4.42

mmol) and freshly dried potassium carbonate (K_2CO_3 , 0.73 g, 5.28 mmol, 1.2 eq) were dissolved in 15 ml of anhydrous dimethylformamide (DMF) under argon atmosphere. The mixture was heated for 30 mins to slight reflux and a solution of 0.74 ml (5.27 mmol, 1.2 eq) of 1-bromohexane was added dropwise via syringe. After complete dropwise addition the reaction was stirred and heated at 100 °C for 18 h. The progress of the reaction was monitored by thin layer chromatography (TLC). The DMF was removed under vacuum distillation and ethyl acetate was added. The organic phase was washed with brine 3 times and dried over anhydrous Na_2SO_4 . The solvents were evaporated on a rotary evaporator and the residue was chromatographed on silica gel (chloroform/hexane = 1:2) to afford **16** as an orange-red solid (1.22g, 89% yield).

1H NMR ($CDCl_3$, 300 MHz, ppm) δ 7.40 (td, J = 8.0, 1.5 Hz, 1H, Ar-H), 7.24 (d, J = 7.8, 1H, Ar-H), 6.84 (dd, J = 7.9, 1.4 Hz, 1H, Ar-H), 3.72 (t, J = 7.4, 2H, N- CH_2), 1.74-1.61 (m, 2H, - CH_2), 1.45-1.25 (m, 6H, - CH_2), 0.90 (t, J = 6.4 Hz, 3H, - CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 180.8, 156.9, 152.4, 138.8, 127.9, 120.9, 115.7, 109.4, 40.2, 31.2, 27.0, 26.4, 22.4, 13.9.

6-bromo-1-hexylindoline-2,3-dione (17a):

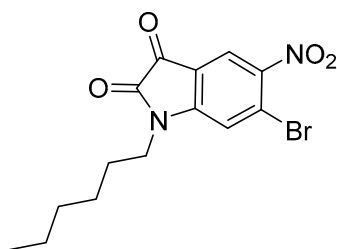


17a was prepared from **14** by a similar synthetic procedure analogous to that of **16**. Compound **17a** was an orange-red solid (81% yield).

1H NMR ($CDCl_3$, 300 MHz) δ 7.45 (d, J = 7.9 Hz, 1H, Ar-H), 7.27 (d, J = 7.7 Hz, 1H, Ar-H), 7.05 (s, 1H, Ar-H), 3.68 (t, J = 7.4 Hz, 2H, N- CH_2), 1.72-1.61 (m, 2H, - CH_2), 1.40-1.30 (m, 6H, - CH_2), 0.88 (t, 3H, J = 6.3 Hz, - CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ 182.4, 157.9, 151.8, 133.5, 126.8, 126.4, 116.2, 113.8, 40.5, 31.3, 27.1, 26.5, 22.5, 13.9.

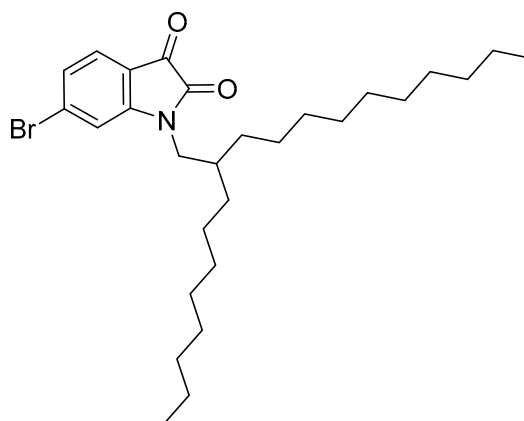
6-bromo-1-hexyl-5-nitroindoline-2,3-dione (17c):



17b was synthesized using by a similar synthetic procedure analogous to that of **16**. Compound **17c** was a yellow solid. (680 mg, 87%).

^1H NMR (CDCl_3 , 300 MHz) δ 8.19 (s, 1H, Ar-H), 7.26 (s, 1H, Ar-H), 3.77 (t, J = 7.4 Hz, 2H, N- CH_2), 1.75-1.67 (m, 2H, $-\text{CH}_2$), 1.40-1.35 (m, 6H, $-\text{CH}_2$), 0.90 (t, 3H, J = 6.3 Hz, $-\text{CH}_3$).

6-bromo-1-(2-octyldodecyl) indoline-2,3-dione (17b):



In an oven-dried round-bottomed flask equipped with a magnetic stir bar, compound **14** (1.39 g, 6.18 mmol) and freshly dried K_2CO_3 (1.70 g, 12.36 mmol, 2 eq) were dissolved in 50 ml of freshly distilled DMF under argon atmosphere. The mixture was warmed at 90 °C for 30 mins and then 2.68 g (7.41 mmol, 1.2eq) of 9-(bromomethyl)nonadecane was added one portion via syringe. The reaction mixture was stirred for overnight at 90 °C. The solution was cooled to room temperature and DMF was removed under vacuum distillation. Then ethyl acetate was added and the organic layer was washed 3 times with water. The organic phase was dried over anhydrous Na_2SO_4 and the solvents were removed by rotational evaporation, the residue was then chromatographed on silica gel (chloroform/hexane = 1:5) to afford **17b** as an orange-red solid (2.65g, 85% yield).

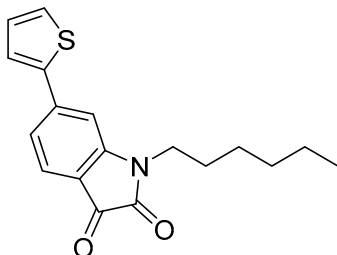
^1H NMR (CDCl_3 , 300 MHz) δ 7.46 (dd, J = 8.0, 2.2 Hz, 1H, Ar-H), 7.27 (d, J = 7.3 Hz, 1H, Ar-H), 7.02 (s, 1H, Ar-H), 3.58 (d, J = 6.7 Hz, 2H, N- CH_2), 1.89-1.76 (m, 1H, N- CH_2 - CH_1), 1.40-1.18 (m, 32H, $-\text{CH}_2$), 0.93 – 0.80 (m, 6H, $-\text{CH}_3$).

^{13}C NMR (CDCl_3 , 75 MHz,) δ 182.3, 158.3, 152.3, 133.5, 126.8, 126.3, 116.2, 114.0, 44.9, 35.9, 31.9,

31.9, 31.4, 29.9, 29.6, 29.6, 29.5, 29.4, 29.3, 26.3, 22.7, 22.7, 14.1.

HRMS (ESI) calculated for $C_{28}H_{45}BrNO_2^+$: 506.2628; Found: 506.2633.

1-hexyl-6-(thiophen-2-yl) indoline-2,3-dione (18a):



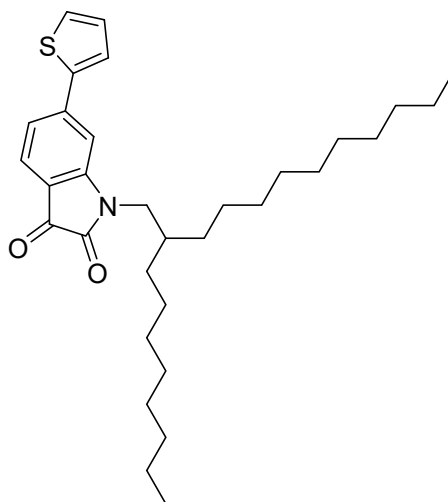
The compound **17a** (1 g, 3.22 mmol) and 2-(tributylstannyl) thiophene (1.68 g, 4.5 mmol, 1.4 eq), were loaded under argon into flask, then an anhydrous DMF (5 mL) was added. After stirring under argon at rt during 0.5 h, $Pd(dppf)Cl_2$ (71 mg, 0.09 mmol, 2%) was added and the solution was warmed to 100 °C. The resulting mixture was stirred at 110 °C overnight. The DMF was removed under vacuum distillation, and the residue was extracted with ethyl acetate. The organic phase was combined and washed with brine, water, and then dried with anhydrous Na_2SO_4 . The solvents were removed by rotational evaporation, the residue was chromatographed on silica gel (chloroform/hexane = 1:2) to afford **18a** as a red solid (0.81g, 80% yield).

1H NMR ($CDCl_3$, 300 MHz) δ 7.60 (d, J = 7.9 Hz, 1H, Ar-H), 7.51-7.45 (m, 2H, Ar-H), 7.34 (d, J = 7.8 Hz, 1H, Ar-H), 7.17 (t, J = 3.9 Hz, 1H, Ar-H), 7.05 (s, 1H, Ar-H), 3.76 (t, J = 7.6 Hz, 2H, N-CH₂), 1.78-1.67 (m, 2H, -CH₂), 1.42-1.28 (m, 6H, -CH₂), 0.91-0.86 (m, 3H, -CH₃).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 182.4, 158.7, 151.8, 144.0, 142.6, 128.7, 128.1, 126.2, 126.1, 120.7, 116.2, 106.8, 40.2, 31.4, 27.3, 26.6, 22.5, 14.0.

HRMS (ESI) calculated for $C_{18}H_{20}NO_2S^+$: 314.1206; Found: 314.1209.

1-(2-octyldodecyl)-6-(thiophen-2-yl) indoline-2,3-dione (18b):



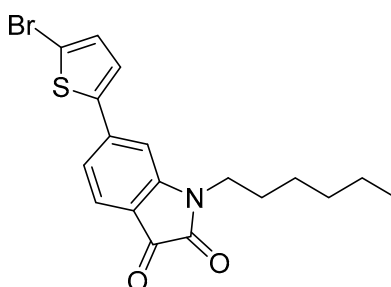
18b was prepared from **17c** by a similar synthetic procedure analogous to that of **18a**. Chromatography on silica gel (chloroform/hexane = 1:3) afford to **18b** as a red solid (1.15 g, 82% yield).

¹H NMR (CDCl₃, 300 MHz) δ 7.61 (d, J = 7.9 Hz, 1H, Ar-H), 7.52-7.44 (m, 2H, Ar-H), 7.35 (d, J = 7.7 Hz, 1H, Ar-H), 7.17 (td, J = 3.9, 2.0 Hz, 1H, Ar-H), 7.06 (s, 1H, Ar-H), 3.64 (d, J = 7.3 Hz, 2H, N-CH₂), 1.93-1.83 (m, 1H, N-CH₂-CH₁), 1.32-1.20 (m, 32H, -CH₂), 0.93-0.88 (m, 6H, -CH₃).

¹³C NMR (CDCl₃, 75 MHz) δ 182.4, 159.0, 152.2, 143.9, 142.6, 128.7, 128.1, 126.2, 125.9, 120.5, 116.2, 107.1, 44.6, 36.2, 31.9, 31.9, 31.6, 29.9, 29.7, 29.6, 29.4, 29.3, 26.5, 22.7, 14.2.

HRMS (ESI) calculated for C₃₂H₄₈NO₂S⁺: 510.3402; Found: 510.3400.

6-(5-bromothiophen-2-yl)-1-hexylindoline-2,3-dione (19a**):**



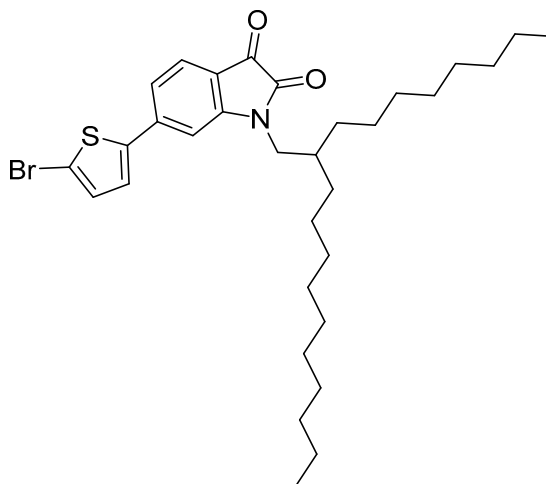
In a round-bottom flask, under argon, the **18a** (50 mg, 0.16 mmol) in THF (3 mL) was added portionwise NBS (32 mg, 0.17 mmol, 1.05 eq) at 0 °C. Then, a catalytic amount of AcOH was added and the suspension was warmed up to room temperature and stirred for 5 h. Water was then added and the solution was extracted three times with dichloromethane. The combined organic layers were dried over anhydrous Na₂SO₄. The solvent was then removed under reduced pressure and the crude product was further purified by chromatographed on silica gel (chloroform/hexane = 1:2 to 1:1) to afford **19a** as an orange solid (51mg, 82% yield).

¹H NMR (CDCl₃, 300 MHz) δ 7.60 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.26-7.21 (m, 2H, Ar-H), 7.12 (d, *J* = 3.7 Hz, 1H, Ar-H), 6.94 (s, 1H, Ar-H), 3.75 (t, *J* = 7.7 Hz, 2H, N-CH₂), 1.75-1.65 (m, 2H, -CH₂), 1.42-1.28 (m, 6H, -CH₂), 0.92-0.85 (m, 3H, -CH₃).

¹³C NMR (CDCl₃, 75 MHz) δ 182.3, 158.6, 151.8, 143.8, 142.9, 131.6, 126.3, 126.2, 120.3, 116.5, 115.3, 106.4, 40.3, 31.4, 27.3, 26.6, 22.5, 14.0.

HRMS (ESI) calculated for C₁₈H₁₉BrNO₂S⁺: 392.0315; Found: 392.0314.

6-(5-bromothiophen-2-yl)-1-(2-octyldodecyl) indoline-2,3-dione (19b):



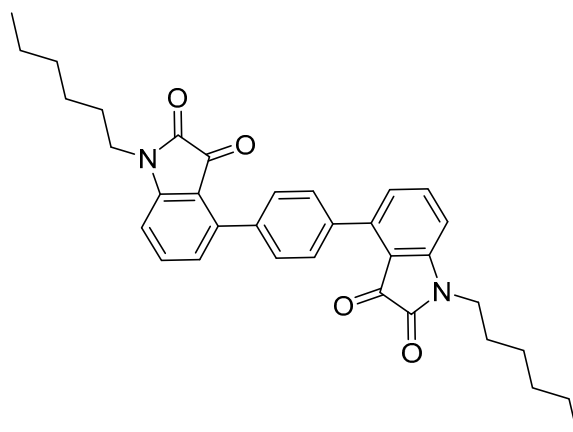
This compound was prepared from **18b** by a similar synthetic procedure analogous to that of **19a**. Chromatography on silica gel (chloroform/hexane = 1:4 to 1:3) afford to **19b** as an orange-red solid (310 mg, 81% yield).

¹H NMR (CDCl₃, 300 MHz) δ 7.60 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.26-7.25 (m, 2H, Ar-H), 7.12 (d, *J* = 4.0 Hz, 1H, Ar-H), 6.94 (s, 1H, Ar-H), 3.63 (d, *J* = 7.3 Hz, 2H, N-CH₂), 1.93-1.82 (m, 1H, N-CH₂-CH₁), 1.44-1.20 (m, 32H, -CH₂), 0.87 (t, *J* = 7.2 Hz, 6H, -CH₃).

¹³C NMR (CDCl₃, 75 MHz) δ 182.3, 158.9, 152.3, 143.9, 142.9, 131.6, 126.2, 126.1, 120.1, 116.5, 115.3, 106.7, 44.6, 36.2, 31.9, 31.9, 31.6, 29.9, 29.7, 29.6, 29.6, 29.4, 29.3, 26.5, 22.7, 22.7, 14.1.

HRMS (ESI) calculated for C₃₂H₄₇BrNO₂S⁺: 588.2505; Found: 588.2505.

4,4'-(1,4-phenylene) bis (1-hexylindoline-2,3-dione) (1):

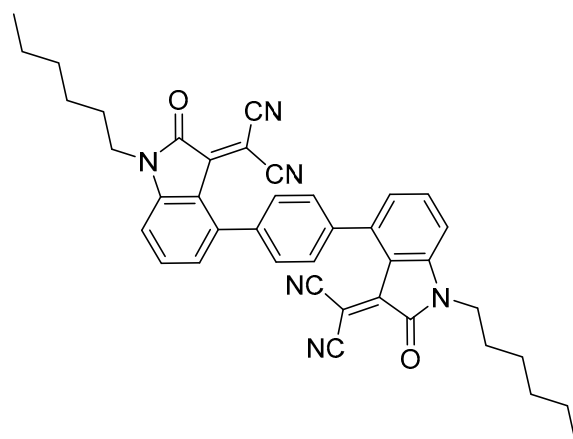


In a round-bottom flask, compound **16** (364 mg, 1.17 mmol), 1,4-Benzenediboronic acid bis (pinacol) ester (193 mg, 0.58 mmol, 0.5 eq), P(o-tyl)₃ (50 mg, 0.17mmol, 10%) and K₃PO₄ (747 mg, 3.52 mmol, 3 eq) were loaded under argon. A solution of toluene (5 mL) and water (0.5 ml) was then added to the flask. After stirring in rt for 0.5 h, Pd₂(dba)₃ (50 mg, 0.05 mmol, 4%) was added and the resulting mixture was heated to 100 °C for overnight. Then, the solvents were removed under vacuum and the reaction crude was extracted with ethyl acetate. The organic phase was combined and washed with brine, water, and then dried with anhydrous Na₂SO₄. After removing the solvent by rotational evaporation, the residue was chromatographed on silica gel (chloroform/hexane = 1:2 to 3:1) to afford **1** as an orange-red solid (160 mg, 52% yield). ¹H NMR (CDCl₃, 300 MHz) δ 7.65-7.58 (m, 6H, Ar-H), 7.17 (dd, *J* = 8.0, 2.0 Hz, 2H, Ar-H), 6.88 (dd, *J* = 8.0, 2.0 Hz, 2H, Ar-H), 3.76 (t, *J* = 7.2, 4H, N-CH₂), 1.77-1.70 (m, 4H, -CH₂), 1.42-1.29 (m, 12H, -CH₂), 0.90 (t, *J* = 6.9, 6H, -CH₃).

¹³C NMR (CDCl₃, 75 MHz) δ 182.3, 157.8, 151.9, 142.7, 137.7, 136.7, 128.9, 125.7, 113.87, 109.0, 40.3, 31.4, 27.2, 26.6, 22.5, 14.0.

HRMS (ESI) calculated for C₃₄H₃₇N₂O₄⁺: 537.2748; Found:537.2747.

2,2'-(1,4-phenylenebis(1-hexyl-2-oxoindoline-4-yl-3-ylidene)) dimalononitrile (2):



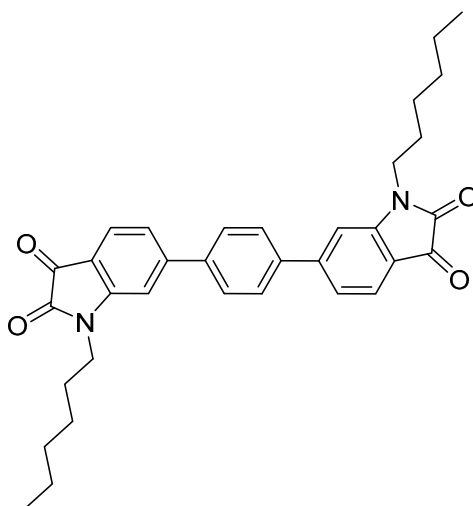
The compound **1** (60 mg, 0.11 mmol) and malononitrile (22 mg, 0.33 mmol, 3 eq) were dissolved in 3.5 ml of anhydrous EtOH. The resulting mixture was warmed to 80 °C and stirred for overnight. Then, the solvent was removed by rotational evaporation and ethyl acetate was added. The organic phase was washed 3 times with water, dried over anhydrous Na₂SO₄. After removing the solvent by rotational evaporation, the residue was chromatographed on silica gel (dichloromethane/hexane = 2:1) to afford **2** as a deep red solid (56 mg, 80% yield).

¹H NMR (CDCl₃, 300 MHz) δ 7.59-7.51 (m, 6H, Ar-H), 7.05 (d, *J* = 7.9 Hz, 2H, Ar-H), 6.82 (d, *J* = 8.0 Hz, 2H, Ar-H), 3.75 (t, *J* = 7.5 Hz, 4H, N-CH₂), 1.75-1.68 (m, 4H, -CH₂), 1.39-1.29 (m, 12H, -CH₂), 0.91 (t, *J* = 6.9, 6H, -CH₃).

¹³C NMR (CDCl₃, 75 MHz) δ 163.1, 147.2, 144.0, 140.0, 136.9, 129.8, 126.5, 116.1, 112.0, 111.0, 108.5, 85.7, 40.7, 31.3, 27.2, 26.6, 22.5, 14.0.

HRMS (ESI) calculated for C₄₀H₃₇N₆O₂⁺: 633.2976; Found: 633.2973.

6,6'-(1,4-phenylene) bis(1-hexylindoline-2,3-dione) (3):



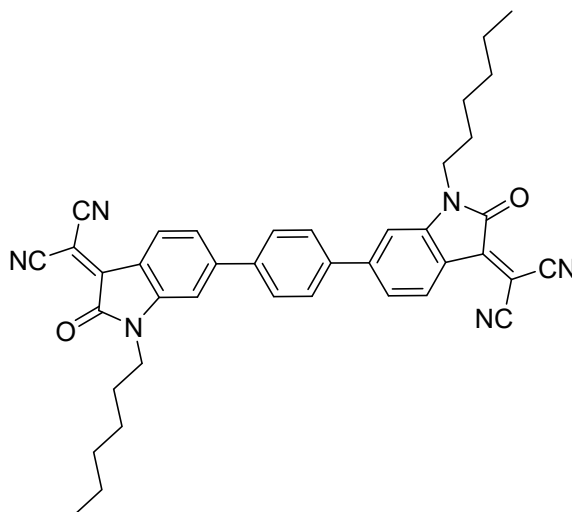
A mixture of **17a** (210 mg, 0.64 mmol), 1,4-Benzenediboronic acid bis (pinacol) ester (96 mg, 0.29 mmol, 0.45 eq), P(o-tyl)₃ (29 mg, 0.09 mmol, 14%) and K₃PO₄ (410 mg, 1.93 mmol, 3 eq) in a solution of toluene (5 mL) and water (0.5 mL), was loaded under argon. The reaction mixture was stirred for 0.5 h, Pd₂(dba)₃ (29 mg, 0.03 mmol, 4%) was then added and refluxed for overnight. The solvents were removed under vacuum distillation. Ethyl acetate was then added, the organic layer was separated and dried over Na₂SO₄. The crude product was chromatographically purified on silica gel eluting with (chloroform/hexane = 1:2 to 4:1) to provide **3** as a red solid (109 mg, 70% yield).

¹H NMR (CDCl₃, 300 MHz) δ 7.76 (s, 4H, Ar-H), 7.71 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.36 (dd, *J* = 7.8, 1.4 Hz, 2H, Ar-H), 7.06 (s, 2H, Ar-H), 3.79 (t, *J* = 7.3 Hz, 4H, N-CH₂), 1.80-1.70 (m, 4H, -CH₂), 1.42-1.29 (m, 12H, -CH₂), 0.89 (t, *J* = 6.9 Hz, 6H, -CH₃).

¹³C NMR (CDCl₃, 75 MHz) δ 182.9, 158.5, 151.7, 150.4, 140.4, 128.1, 126.0, 122.4, 116.7, 108.6, 40.3, 31.4, 27.4, 26.6, 22.5, 14.0.

HRMS (ESI) calculated for C₃₄H₃₇N₂O₄⁺: 537.2748; Found: 537.2748.

2,2'-(1,4-phenylenebis(1-hexyl-2-oxoindoline-6-yl-3-ylidene)) dimalononitrile (4):



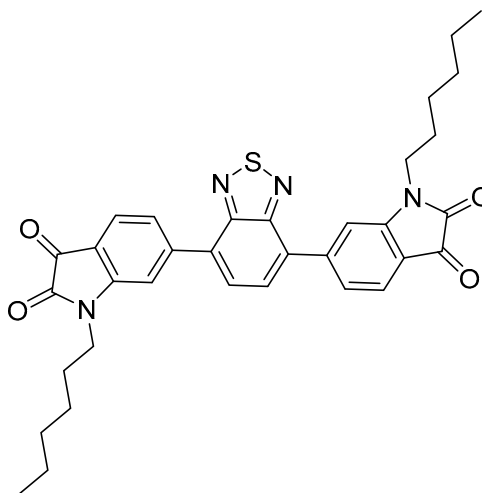
This compound was prepared from **3** by a similar synthetic procedure analogous to that of **2**. The crude was purified by chromatography on silica gel (dichloromethane/ petroleum ether = 2:1) to afford **4** as a red solid (50mg, 88% yield).

¹H NMR (CDCl₃, 300 MHz) δ 8.22 (dd, *J* = 8.2, 2.5 Hz, 2H, Ar-H), 7.78 (s, 4H, Ar-H), 7.39 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.06 (s, 2H, Ar-H), 3.79 (t, *J* = 7.6 Hz, 4H, N-CH₂), 1.78-1.66 (m, 4H, -CH₂), 1.42-1.28 (m, 12H, -CH₂), 0.89 (t, *J* = 6.9 Hz, 6H, -CH₃).

¹³C NMR (CDCl₃, 75 MHz) δ 162.7, 149.5, 148.6, 147.4, 140.3, 128.1, 127.4, 122.4, 117.7, 112.5, 108.0, 81.9, 40.6, 31.4, 27.4, 26.6, 22.5, 14.0.

HRMS (ESI) calculated for C₄₀H₃₇N₆O₂⁺: 633.2976; Found: 633.2973.

6,6'-(benzo[*c*] [1,2,5] thiadiazole-4,7-diyl) bis (1-hexylindoline-2,3-dione) (5):



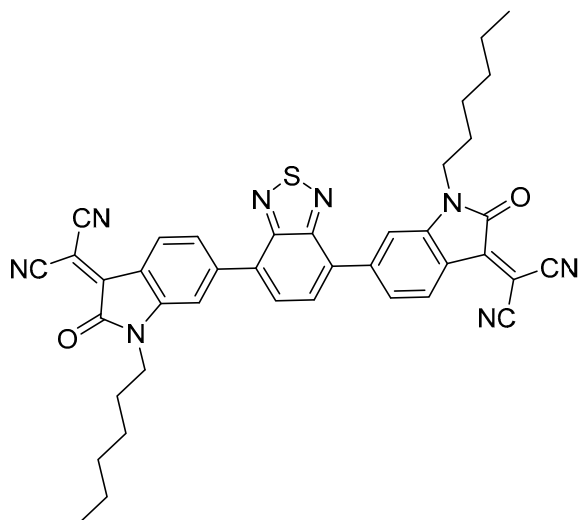
A mixture of compound **17a** (300 mg, 0.97 mmol), 2,1,3-Benzothiadiazole-4,7-diboronic acid bis(pinacol) ester (170 mg, 0.44 mmol, 0.45 eq), P(o-tyl)₃ (40 mg, 0.13 mmol, 14%), K₃PO₄ (617 mg, 2.91 mmol, 3 eq), toluene (2.5 mL) and water (0.5 mL) were loaded in a flask and purged with argon. After stirring in rt for 0.5 h, Pd₂(dba)₃ (40 mg, 0.04 mmol, 4%) was added and refluxed for overnight. Solvents were removed, the crude was extracted with ethyl acetate and dried over anhydrous Na₂SO₄. The crude was chromatographed on silica gel (chloroform/hexane = 3:2) to afford **5** as a red solid (145 mg, 55% yield).

¹H NMR (CDCl₃, 300 MHz) δ 7.95 (s, 2H, Ar-H), 7.78 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.64 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.62 (s, 2H, Ar-H), 3.82 (t, *J* = 7.3 Hz, 4H, N-CH₂), 1.84-1.74 (m, 4H, -CH₂), 1.44-1.28 (m, 12H, -CH₂), 0.89 (t, *J* = 7.1 Hz, 6H, -CH₃).

¹³C NMR (CDCl₃, 75 MHz) δ 183.1, 158.3, 153.5, 151.2, 146.6, 133.3, 128.7, 125.6, 124.3, 117.2, 111.4, 40.4, 31.4, 27.3, 26.6, 22.5, 14.0.

HRMS (ESI) calculated for C₃₄H₃₅N₄O₄S⁺: 595.2373; Found: 595.2374.

2,2'-(benzo[c][1,2,5]thiadiazole-4,7-diylbis(1-hexyl-2-oxoindoline-6-yl-3-ylidene))dimalononitrile (6):



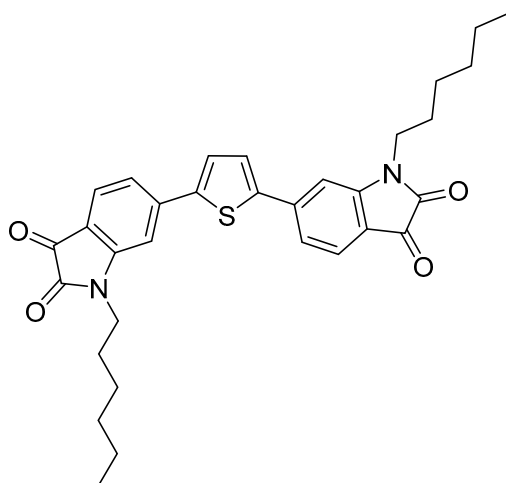
This compound was prepared from **5** by a similar synthetic procedure analogous to that of **2**. The crude was purified by chromatography on silica gel (dichloromethane/petroleum ether = 3:1) afforded **6** as a red solid (27 mg, 80% yield).

¹H NMR (CDCl₃, 300 MHz) δ 8.29 (d, J = 8.1 Hz, 2H, Ar-H), 7.98 (s, 2H, Ar-H), 7.68 (d, J = 7.9 Hz, 2H, Ar-H), 7.65 (s, 2H, Ar-H), 3.81 (t, J = 7.3 Hz, 4H, N-CH₂), 1.82-1.68 (m, 4H, -CH₂), 1.44-1.29 (m, 12H, -CH₂), 0.89 (t, J = 7.2 Hz, 6H, -CH₃).

¹³C NMR (CDCl₃, 75 MHz) δ 162.6, 153.5, 148.7, 146.9, 145.8, 133.1, 128.7, 127.1, 124.2, 118.3, 112.4, 110.9, 82.5, 40.7, 31.4, 27.3, 26.6, 22.5, 14.0.

HRMS (ESI) calculated for C₄₀H₃₅N₈O₂S⁺: 691.2600; Found: 691.2598.

6,6'-(thiophene-2,5-diyl) bis(1-hexylindoline-2,3-dione) (7a):



A mixture of compound **17a** (90 mg, 0.29 mmol), 2,5-Bis(tributylstannyl)thiophene (88 mg, 0.13 mmol, 0.45 eq), and anhydrous dimethylformamide (2 mL) was loaded in a flask and purged with argon. After stirred in rt for 0.5 h, Pd(dppf)Cl₂ (15 mg, 0.02 mmol, 6%) was added and refluxed overnight. DMF was removed under vacuum distillation, the residue was extracted

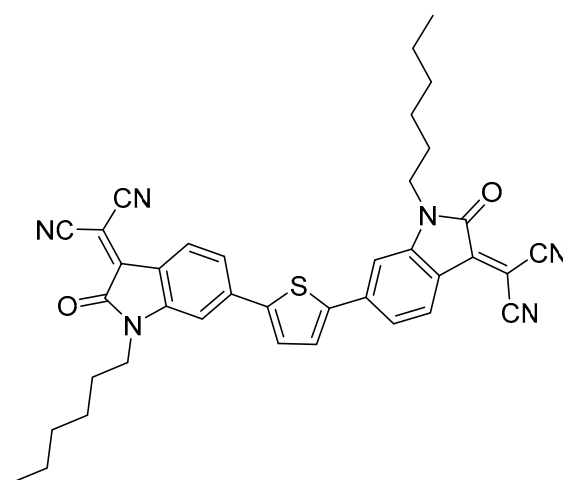
with ethyl acetate, dried over Na₂SO₄ and chromatographed on silica gel (dichloromethane/hexane = 1:1) to afford **7a** as a red solid (44 mg, 64% yield).

¹H NMR (CDCl₃, 300 MHz) δ 7.65 (d, *J* = 7.7 Hz, 2H, Ar-H), 7.55 (s, 2H, Ar-H), 7.39 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.08 (s, 2H, Ar-H), 3.79 (t, *J* = 7.4 Hz, 4H, N-CH₂), 1.80-1.70 (m, 4H, -CH₂), 1.44-1.30 (m, 12H, -CH₂), 0.90 (t, *J* = 7.1 Hz, 6H, -CH₃).

¹³C NMR (CDCl₃, 75 MHz) δ 182.3, 158.5, 151.8, 144.5, 142.9, 127.3, 126.3, 120.7, 116.8, 106.6, 40.3, 31.4, 27.3, 26.6, 22.5, 14.0.

HRMS (ESI) calculated for C₃₂H₃₅N₂O₄S⁺:543.2310; Found: 543.2312.

2,2'-(thiophene-2,5-diylbis(1-hexyl-2-oxoindoline-6-yl-3-ylidene)) dimalononitrile (8a):



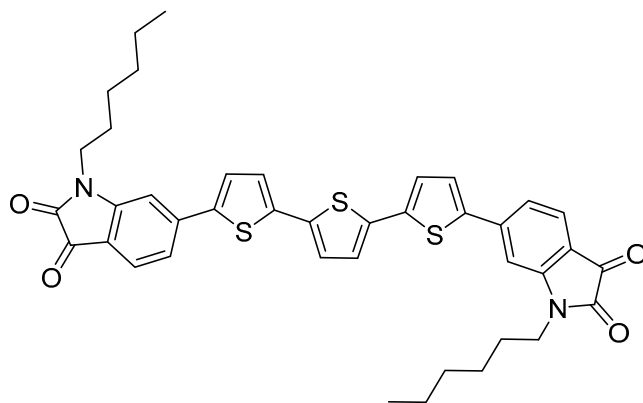
The compound **7a** (20 mg, 0.03 mmol) and malononitrile (8 mg, 0.11 mmol, 3 eq) were dissolved in 3.0 ml of anhydrous EtOH. Followed by the addition of 2 drops of pyridine by syringe. C. The mixture was then stirred overnight at room temperature. On completion, the solvent was removed by rotational evaporation and chloroform was added. The organic phase was washed 3 times with water, dried over anhydrous Na₂SO₄. The crude was purified by chromatography on silica gel (dichloromethane/petroleum ether = 1:2) to afford **8a** as a deep-red solid (17 mg, 89% yield).

¹H NMR (CDCl₃, 300 MHz) δ 8.15 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.59 (s, 2H, Ar-H), 7.40 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.05 (s, 2H, Ar-H), 3.77 (t, *J* = 6.9 Hz, 4H, N-CH₂), 1.78-1.68 (m, 4H, -CH₂), 1.42-1.30 (m, 12H, -CH₂), 0.90 (t, *J* = 7.1 Hz, 6H, -CH₃).

¹³C NMR (CDCl₃, 75 MHz) δ 162.8, 147.9, 147.4, 144.9, 142.0, 127.6, 120.6, 117.9, 112.6, 110.8, 106.0, 81.4, 40.6, 31.3, 27.4, 26.5, 22.5, 14.0.

HRMS (ESI) calculated for C₃₈H₃₅N₆O₂S⁺:639.2542; Found: 639.2537.

6,6'-([2,2':5',2''-terthiophene]-5,5''-diyl) bis(1-hexylindoline-2,3-dione) (9a):



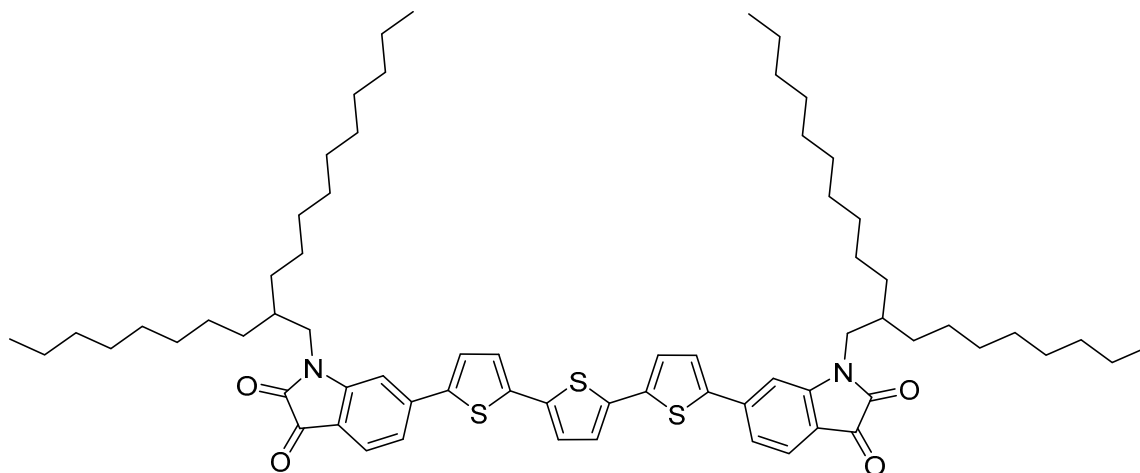
This compound was prepared from **19a** (150 mg, 0.38 mmol), 2,5-Bis(tributylstannyl)thiophene (105 mg, 0.15 mmol, 0.40 eq), DMF (5 mL) and Pd(dppf)Cl₂ (15 mg, 0.02 mmol, 5%) as described for **7a**. The crude was purified on silica gel (dichloromethane/hexane = 1:1 to 2:1) to afford **9a** as a red solid (83 mg, 75% yield).

¹H NMR (CDCl₃, 300 MHz) δ 7.62 (dd, *J* = 8.2, 3.7 Hz, 2H, Ar-H), 7.45 (d, *J* = 3.7 Hz, 2H, Ar-H), 7.32 (dd, *J* = 7.5, 2.9 Hz, 2H, Ar-H), 7.24 (d, *J* = 3.1 Hz, 2H, Ar-H), 7.22 (s, 2H, Ar-H), 7.03 (s, 2H, Ar-H), 3.78 (t, *J* = 7.6 Hz, 4H, N-CH₂), 3.78-3.72 (m, 4H, -CH₂), 1.42-1.32 (m, 12H, -CH₂), 0.95-0.84 (m, 6H, -CH₃).

¹³C NMR (CDCl₃, 75 MHz) δ 182.2, 158.7, 151.8, 143.3, 141.4, 139.3, 136.4, 127.1, 126.2, 125.5, 125.3, 120.2, 116.3, 106.2, 40.2, 31.4, 27.4, 26.6, 22.5, 14.0.

HRMS (ESI) calculated for C₄₀H₃₉N₂O₄S₃⁺: 707.2059; Found: 707.2066.

6,6'-([2,2':5',2''-terthiophene]-5,5''-diyl)bis(1-(2-octyldodecyl)indoline-2,3-dione) (9b):



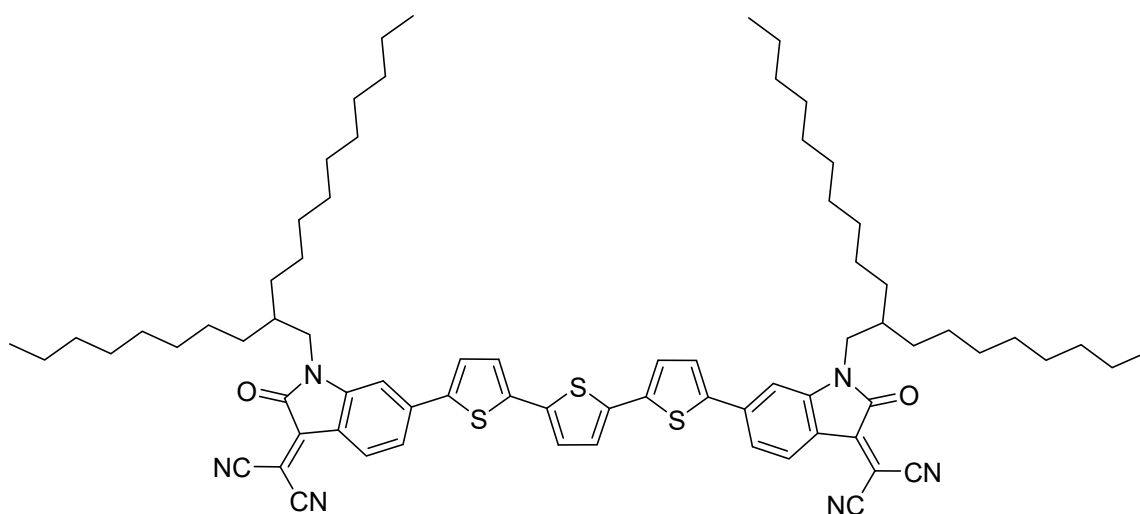
This compound was prepared from **19b** (42 mg, 0.07 mmol), 2,5-Bis(tributylstannyl) thiophene (20 mg, 0.03 mmol, 0.42 eq), DMF (2.5 mL) and Pd(dppf)Cl₂ (8 mg, 0.01 mmol, 14%) as described for **7a**. The crude was purified on silica gel (ethyl acetate/hexane = 1:3 to 4:1) to afford **9b** as a red solid (15 mg, 50% yield).

¹H NMR (CDCl₃, 300 MHz) δ 7.62 (dd, *J* = 8.1, 1.4 Hz, 2H, Ar-H), 7.43 (d, *J* = 3.3 Hz, 2H, Ar-H), 7.33 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.24 (d, *J* = 3.2 Hz, 2H, Ar-H), 7.21 (s, 2H, Ar-H), 7.04 (s, 2H, Ar-H), 3.66 (d, *J* = 7.1 Hz, 4H, N-CH₂), 1.94-1.82 (m, 2H, N-CH₂-CH₁), 1.38-1.22 (m, 64H, -CH₂), 0.92-0.86 (m, 12H, -CH₃).

¹³C NMR (CDCl₃, 75 MHz) δ 182.2, 152.2, 141.4, 139.3, 136.4, 127, 126.2, 125.5, 125.3, 120.1, 116.3, 106.5, 44.6, 36.2, 31.9, 31.9, 31.6, 30.0, 29.7, 29.4, 29.4, 28.3, 26.6, 22.7, 14.2, 13.6.

HRMS (ESI) calculated for C₆₈H₉₅N₂O₄S₃⁺: 1099.6450; Found: 1099.6448.

2,2'-([2,2':5',2''-terthiophene]-5,5''-diylbis(1-(2-octyldodecyl)-2-oxoindoline-6-yl-3-ylidene)) dimalononitrile (10b):



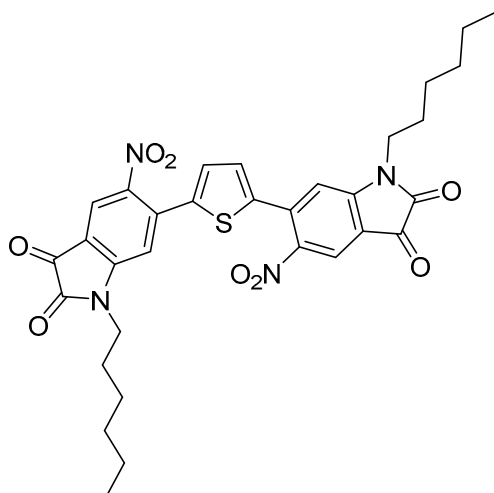
This compound was prepared from **9b** (10 mg) and malononitrile (2 mg) in 1 ml of dry EtOH and 1 ml of DCM as described for **2**. The crude was purified by chromatography on silica gel (dichloromethane/petroleum ether = 1:1) to afford **10b** as a deep blue solid (10mg, 95% yield).

¹H NMR (CDCl₃, 300 MHz) δ 8.11 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.47 (d, *J* = 4.0 Hz, 2H, Ar-H), 7.34 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.25 (d, *J* = 3.1 Hz, 2H, Ar-H), 7.22 (s, 2H, Ar-H), 6.98 (s, 2H, Ar-H), 3.63 (d, *J* = 7.1 Hz, 4H, N-CH₂), 1.91-1.81 (m, 2H, N-CH₂-CH₁), 1.43-1.18 (m, 64H, -CH₂), 0.91-0.87 (m, 12H, -CH₃).

¹³C NMR (CDCl₃, 75 MHz) δ 163.3, 147.9, 147.7, 142.4, 141.5, 139.8, 136.5, 127.5, 125.7, 125.5, 120.0, 117.1, 112.9, 111.1, 105.8, 80.3, 44.9, 36.4, 31.9, 31.9, 31.6, 30.0, 29.7, 29.6, 29.4, 29.4, 26.6, 22.7, 14.2.

HRMS (APPI) calculated for C₇₄H₉₅N₂O₆S₃⁺: 1195.6673; Found: 1195.6653.

6,6'-(thiophene-2,5-diyl) bis(1-hexyl-5-nitroindoline-2,3-dione) (7b):



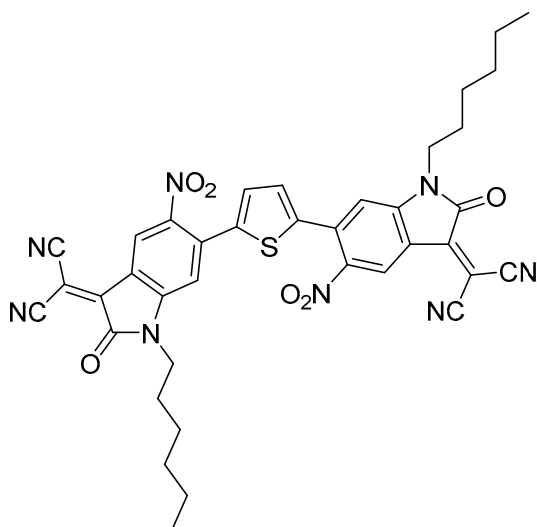
This compound was prepared from **17b** (210 mg, 0.59 mmol), 2,5-Bis(tributylstannyl)thiophene (163 mg, 0.25 mmol, 0.49 eq), DMF 2 mL and Pd(dppf)Cl₂ (21 mg, 0.03 mmol, 5%) as described for **7a**. The crude was purified on silica gel (dichloromethane/hexane = 2:1) to afford **7b** as a red solid (140 mg, 90% yield).

¹H NMR (CDCl₃, 300 MHz) δ 8.16 (s, 2H, Ar-H), 7.22 (s, 2H, Ar-H), 7.04 (s, 2H, Ar-H), 3.82 (t, *J* = 7.3 Hz, 4H, N-CH₂), 1.76-1.69 (m, 4H, -CH₂), 1.40-1.34 (m, 12H, -CH₂), 0.91-0.86 (m, 6H, -CH₃).

¹³C NMR (CDCl₃, 75 MHz) δ 180.8, 157.7, 152.8, 144.6, 139.8, 137.8, 129.4, 122.1, 116.4, 113.1, 40.9, 31.3, 27.3, 26.5, 22.5, 14.0.

HRMS (ESI) calculated for C₃₂H₃₃N₄O₈S⁺:633.2013; Found: 633.2014.

2,2'-(thiophene-2,5-diylbis(1-hexyl-5-nitro-2-oxoindoline-6-yl-3-ylidene))dimalononitrile (8b):



This compound was prepared from **7b** (30 mg, 0.04 mmol), malononitrile (10 mg, 0.14 mmol, 3.5 eq) and 3 ml of anhydrous EtOH as described for **2**. The crude was purified on silica gel (dichloromethane/ petroleum ether = 1:1) to afford **8b** as a deep red solid (29 mg, 85% yield).

¹H NMR (CDCl₃, 300 MHz) δ 8.62 (s, 2H, Ar-H), 7.24 (s, 2H, Ar-H), 7.00 (s, 2H, Ar-H), 3.82 (t, *J* = 7.4 Hz, 4H, N-CH₂), 1.74-1.69 (m, 4H, -CH₂), 1.40-1.34 (m, 12H, -CH₂), 0.92-0.86 (m, 6H, -CH₃).

¹³C NMR (CDCl₃, 75 MHz) δ 162.2, 148.4, 146.5, 144.4, 140.0, 136.6, 129.8, 123.0, 117.6, 112.2, 111.5, 109.8, 85.7, 41.2, 31.2, 27.3, 26.5, 22.46, 14.0.

HRMS (ESI) calculated for C₃₈H₃₃N₈O₆S⁺: 729.2245; Found: 729.2238.

3. UV-vis absorption spectra

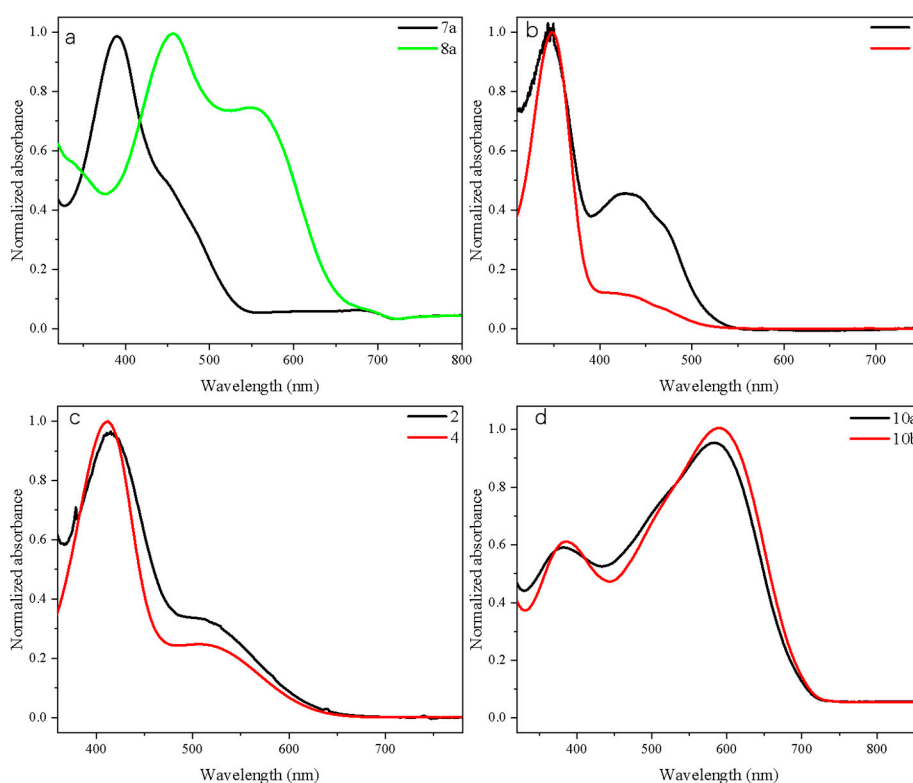


Figure S1. Normalized UV-vis absorption spectra of (a) Compound **7a** and **8a** in THF; (b) bis-isatin compounds **1** and **3** in THF; (c) di-2-(2-oxindolin-3-ylidene) malononitrile compounds **2** and **4** in THF; (d) di-2-(2-oxindolin-3-ylidene) malononitrile compounds **10a** and **10b** in THF.

The introduction of dicyano groups (malononitrile compounds) leads to a red shift of the maximum absorption peak by about 100 nm as shown in Fig. a. Based on Figs. b and c for the materials based on benzene ring as a bridging group, the position of the substituent group does not have a significant effect on the position of the absorption peaks but mainly affects the intensity of their ICT peaks at the same molecular composition. As shown in Fig. d, changing the substituent at the N position with different alkyl chain lengths has almost no effect on the absorption spectrum.

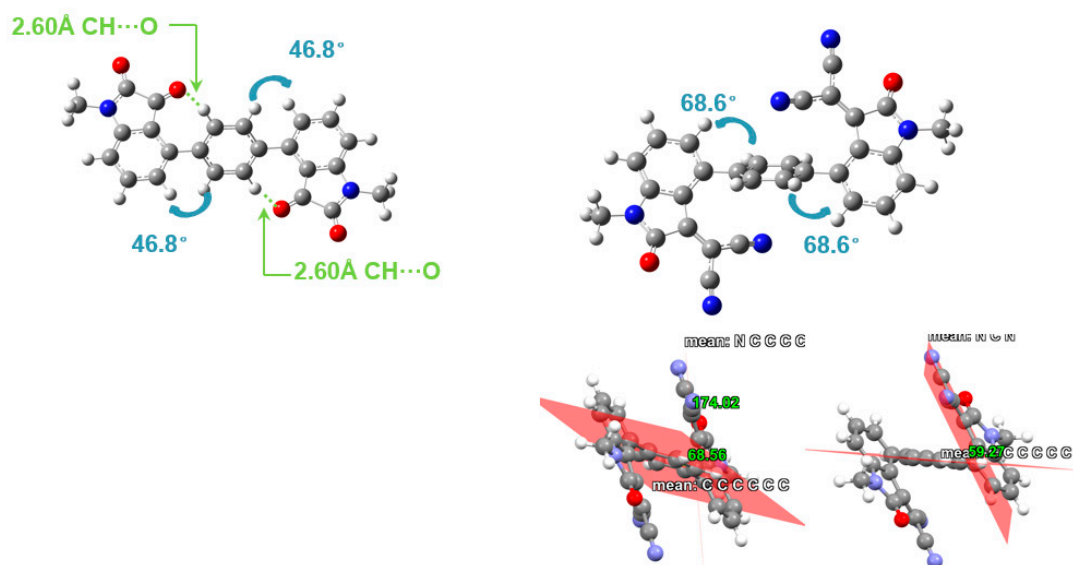
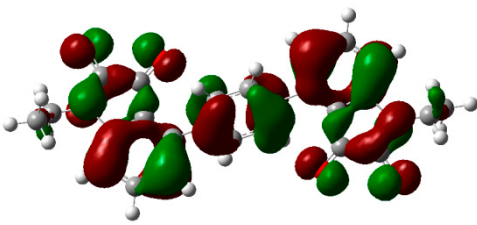
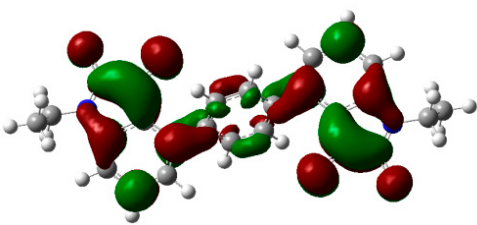
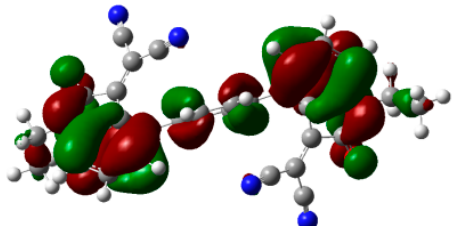
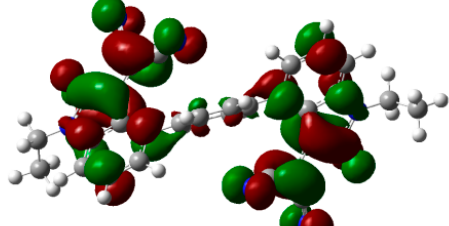
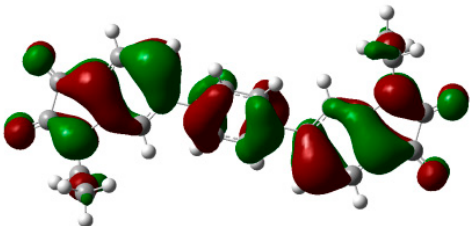
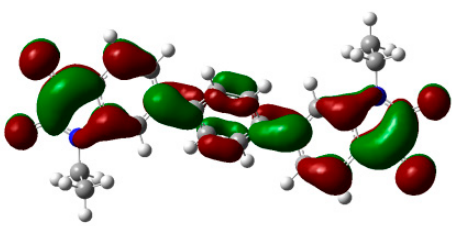
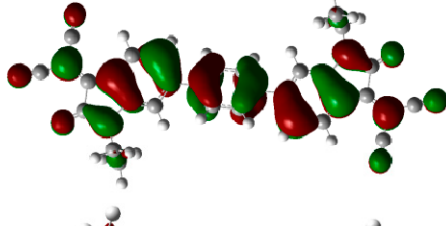
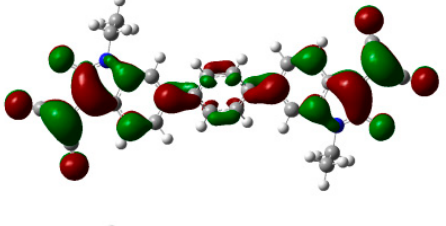
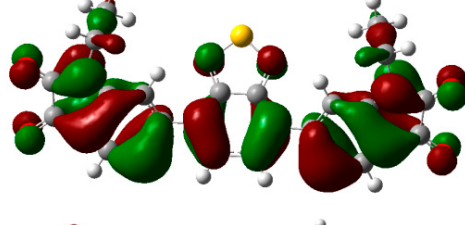
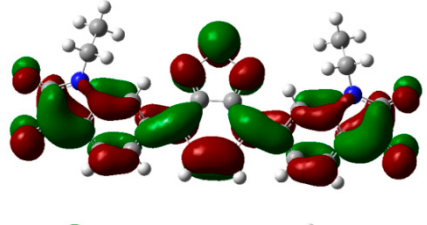
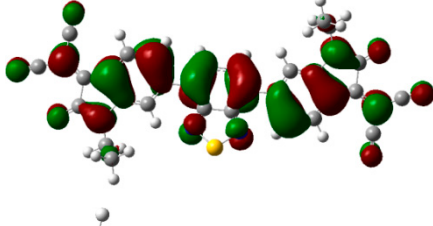
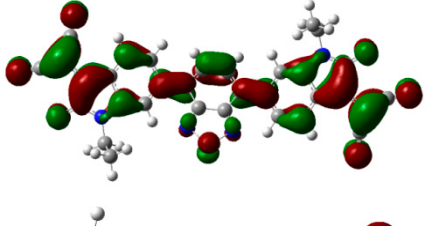
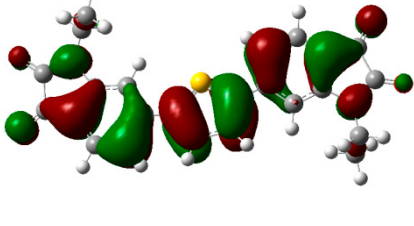
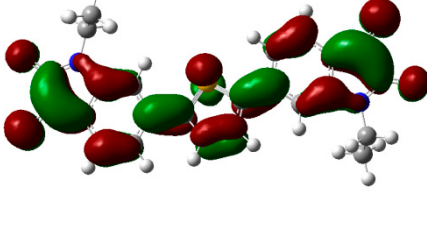


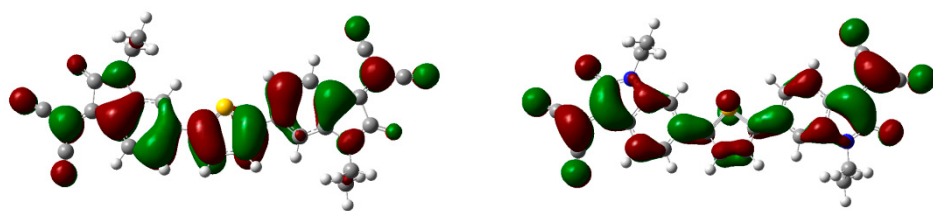
Figure S2. The lowest energy configuration of compound 1 and 2 obtained by relying on DFT at the B3LYP-D3/def2tzvp level.

Based on the results of the theoretical simulations, it can be seen that the planarity of material 1 is better. While the molecular co-planarity of material 2 is relatively poor, which is related to the space site resistance with the benzene ring caused by the length of the cyano group.

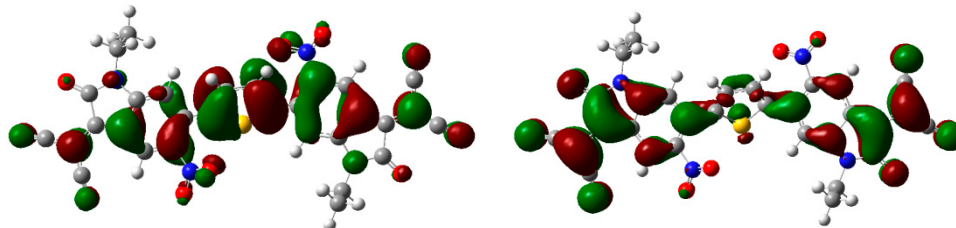
5. Figure S3. HOMO/LUMO maps of bis-isatin and di-2-(2-oxindolin-3-ylidene) malononitrile derivatives.

Acronym	HOMO map	LUMO map
1		
2		
3		
4		
5		
6		
7a		

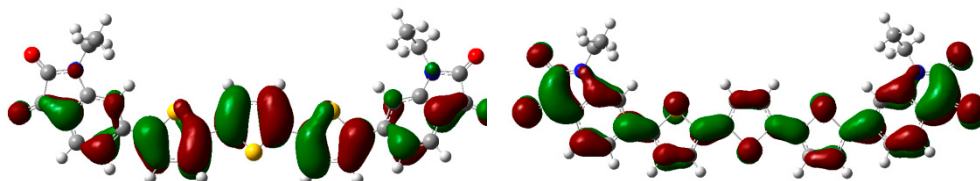
8a



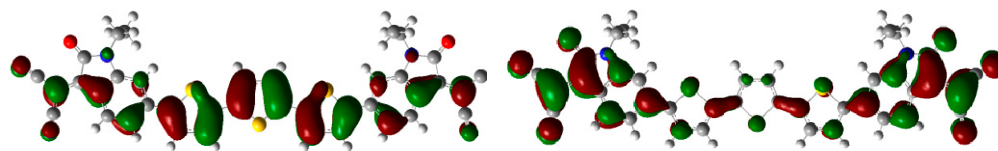
8b



9



10



6. Device fabrication

6.1. Perovskite solar cells fabrication

The inverted planer heterojunction structure solar cells were fabricated under N₂ atmosphere conditions and started from ITO/PEDOT:PSS. The (MA_{0.17}FA_{0.83})_{0.95}Cs_{0.05}Pb(I_{0.83}Br_{0.17})₃ perovskite precursor solution was spin-coated onto the substrate via a two-step speed process at 2000 rpm for 10 s and 4000 rpm for 30 s, respectively. During the second spin-coating step, 100 µL of chlorobenzene (CB) was dropped onto the substrate. The resulting film was then annealed at 100 °C for 30 min for enhanced crystallization. Afterwards, PCBM as reference or **10a** as electron transport layers were spin-coated on perovskite layer, without further annealing. Finally, BCP (5 nm), used as hole blocking layer, was evaporated and deposited onto the ETL and, a thick contact layer of Ag (100 nm) was used as top electrode by using this thermal evaporator condition under vacuum (6×10⁻⁶ mbar) through a shadow mask to define the active area (0.28 cm²) of the devices.

6.2. Preparation of ITO substrates

Pre-patterned indium-tin oxide (ITO) coated glass slides of 1.5 x 2 cm² with a sheet resistance of $R_s = 7 \Omega \cdot \text{sq}^{-1}$ were provided at our own lab (LPICM) from Sputtering - Alliance concept Systems. To remove the contaminants from the ITO surface, were cleaned in ultrasonic baths for 15 minutes for each step in the following order: deionized water with detergent (2 drops of Deconex® 12 PA-x solution), then acetone and finally isopropanol and were dried with nitrogen gun. Eventually, the UV-ozone treatment was performed for 15 minutes ensuring elimination of residual organic contaminants of the ITO substrates.

6.3. Deposition of PEDOT:PSS

A filtered aqueous solution of poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate) (purchased from Ossila, Al 4083) through the PVDF (hydrophilic / 45 µm) filter is dispensed on the ITO substrate at room temperature and then spun-cast at 4500 rpm for 40 s. Then, the edge parts of the conductive polymer film are removed by cotton swabs before being baked. The last step, the PEDOT:PSS deposit samples are annealed at 120°C for 30 minutes outside the glovebox. After the PEDOT:PSS films are introduced in the glovebox to avoid any reabsorption of water from the atmosphere.

6.4. Preparation of Triple Cation Perovskite Precursor Solution

The triple cation perovskite solution (MA_{0.17}FA_{0.83})_{0.95}Cs_{0.05}Pb(I_{0.83}Br_{0.17})₃ was prepared by mixing a precursor solution of formamidinium iodide (1 M), methylammonium bromide (0.2 M), lead iodide (1.1 M) and lead bromide (0.2) in a mixture of DMSO/DMF (1:4) solvent system. Then by adding 1.5 molar ratio of CsI (dissolved in DMSO) solution. The perovskite precursor solution was stirred at room temperature under a N₂ atmosphere between 4 to 5 h before use.

6.5. Preparation of the PCBM (Reference ETL)

The PCBM solution was made by dissolving 20 mg of PCBM in 1 mL of anhydrous CB and stirred for 4 or 5 h at 70°C. The solution was spin-coated onto the perovskite film and spin-coated 6000 rpm for 30 s.

6.6. Preparation of the 10a solution (ETL)

Have prepared by adding the 5 mg of **10a** in 2 mL of CB and stirred for 2 h at 60°C. The solution was spin-coated onto the perovskite film at 1000 rpm for 30 s.

6.7. Preparation of the 4 solution (passivating agent)

The **4** solution was made by dissolving 3 mg in 1 mL of CB and stirred for 2 h at 70°C. The solution was spin-coated as an antisolvent /or passive treatment onto the perovskite films, eg., following this condition: perovskite precursor solution was spin-coated onto the substrate via a two-step speed process at 2000 rpm for 10 s and 4000 rpm for 30 s, respectively. During the second spin-coating step, 100 μ L of **4** solution was dropped onto the substrate. The resulting film was then annealed at 100 °C for 30 min for enhanced crystallization.

6.8. Space charge limited current (SCLC) device fabrication

To evaluate the electron mobility of **10a**, we fabricated electron-only devices with the structures of ITO/SnO₂/**10a**/LiF/Al and performed SCLC measurements. According to the charge behaviour, the *J-V* log-log plots can be divided into three regions: ohmic region, trap-filled limited (TFL) region, SCLC region.

6.9. Preparation of SnO₂ nanoparticle solution by sol-gel method

The precursor solution of SnO₂ (0.1 M) was obtained by dissolving 112.8 mg precursor of tin (SnCl₂·2H₂O) in 5 mL absolute ethanol and then SnO₂ solution stirred 6h at 80 °C. After the solution kept at room temperature for at least 1 day, allowing the aging process. Afterward, we used this solution for preparing SnO₂ films by spin-coating without any purification at a speed rate of 3000 rpm for 40 s and have thermal annealing at 180 °C for 1 h on hot plate.

6.10. Preparation of the 10a solution (SCLC fabrication)

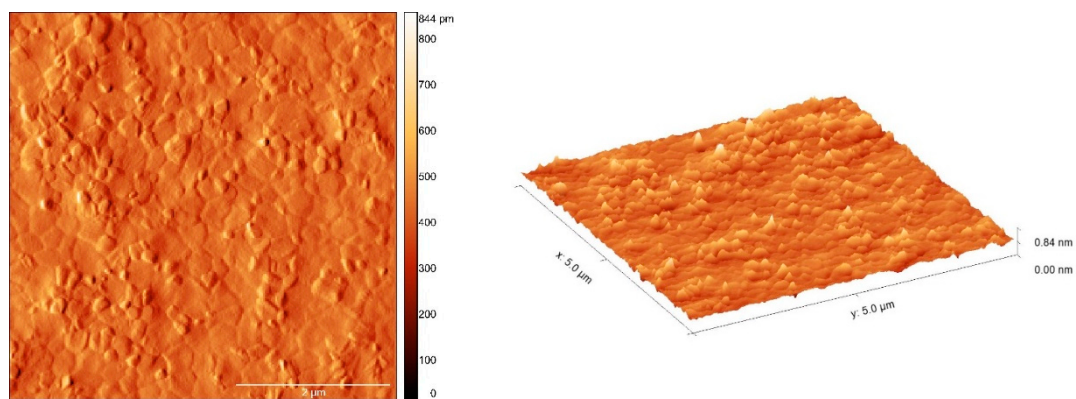
The **10a** solution was made by dissolving 5 mg in 1 mL of CB and stirred for 4 or 5 h at 70°C. The solution was spin-coated onto the SnO₂ films and spin-coated 2000 rpm for 30 s and the thickness determined with profilometer around 88 nm.

6.11. Deposition of LiF and Al

LiF can be used as cathode interlayer to favor electron extraction. LiF and Al layers were deposited by vacuum evaporation to reach thicknesses of 7 and 100 nm, respectively (under a pressure of 10⁻⁷ mbar at an evaporation rate of ca. 0.4 Å/s).

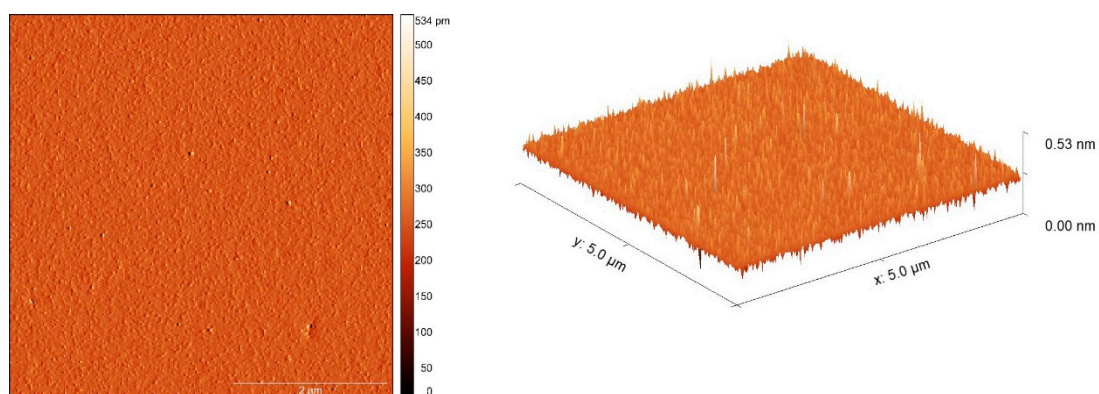
7. **Figure S4.** AFM image of PSCs device (a) and SCLC device for measuring the electron mobility (b).

a)



ITO/PEDOT PSS/3CP/10a/BCP

b)



ITO/SnO₂/10a/LiF

8. Mass spectra

Figure S5. Mass spectra of Compound 1.

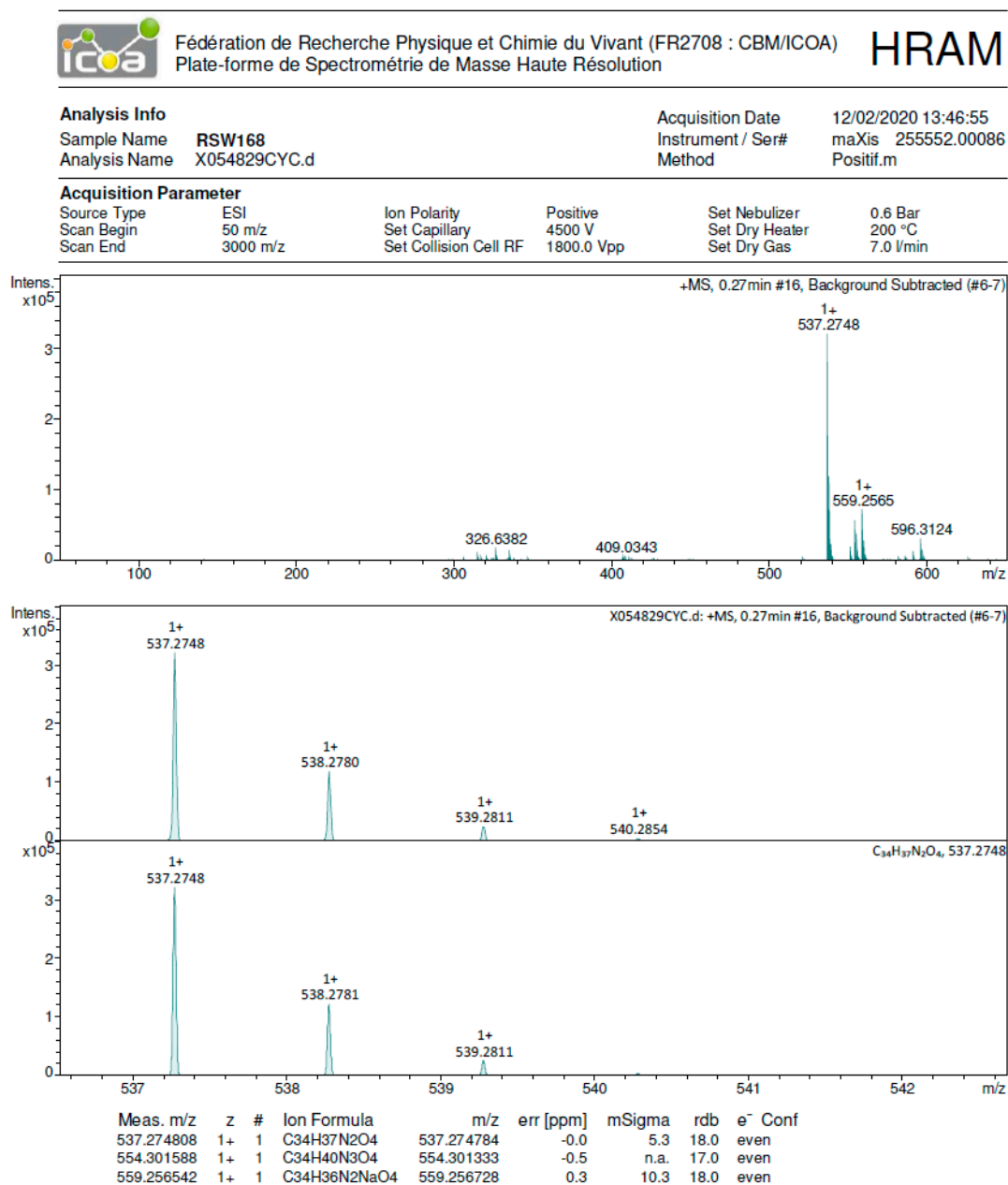
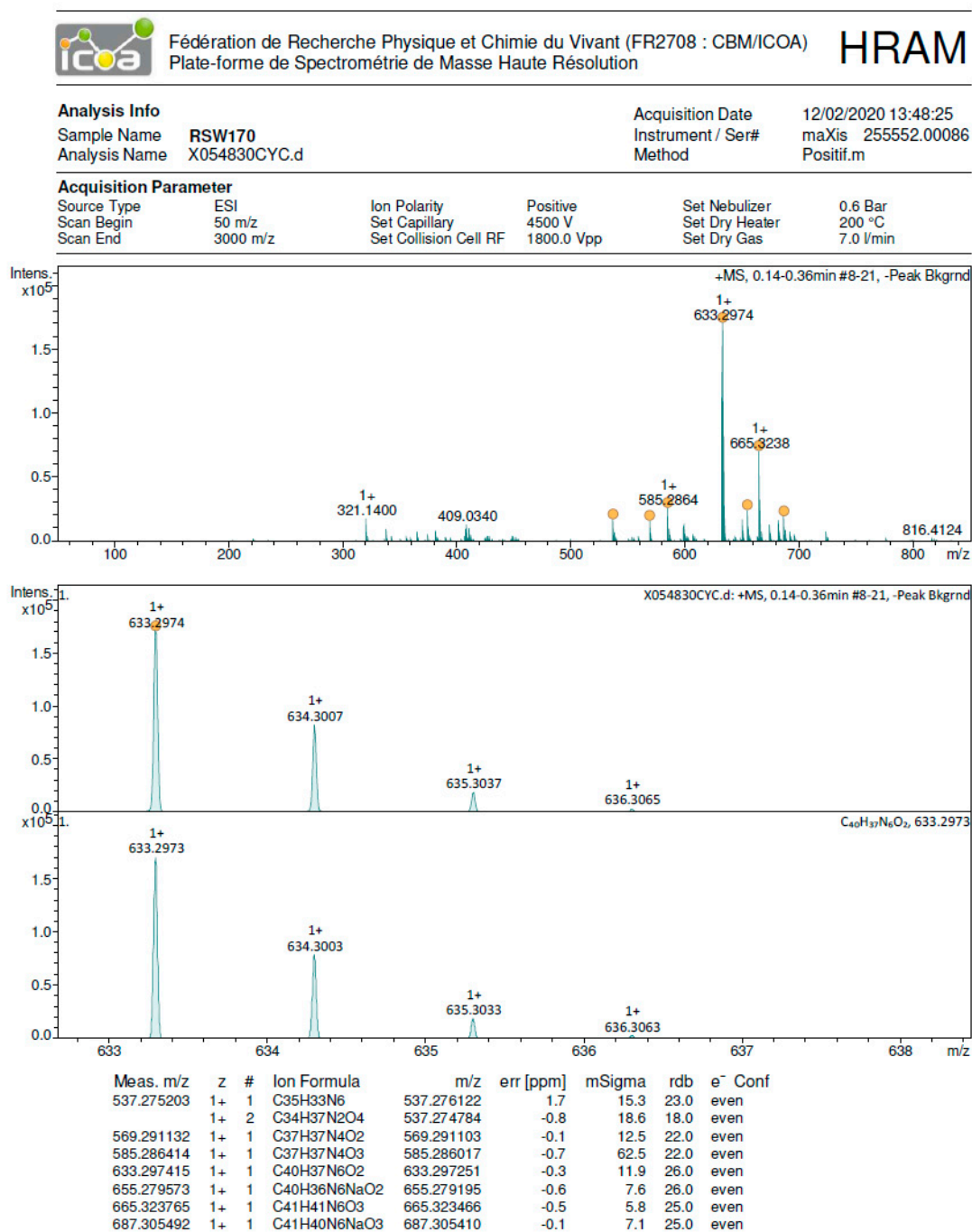


Figure S6. Mass spectra of Compound 2.



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Figure S7. Mass spectra of Compound 3.

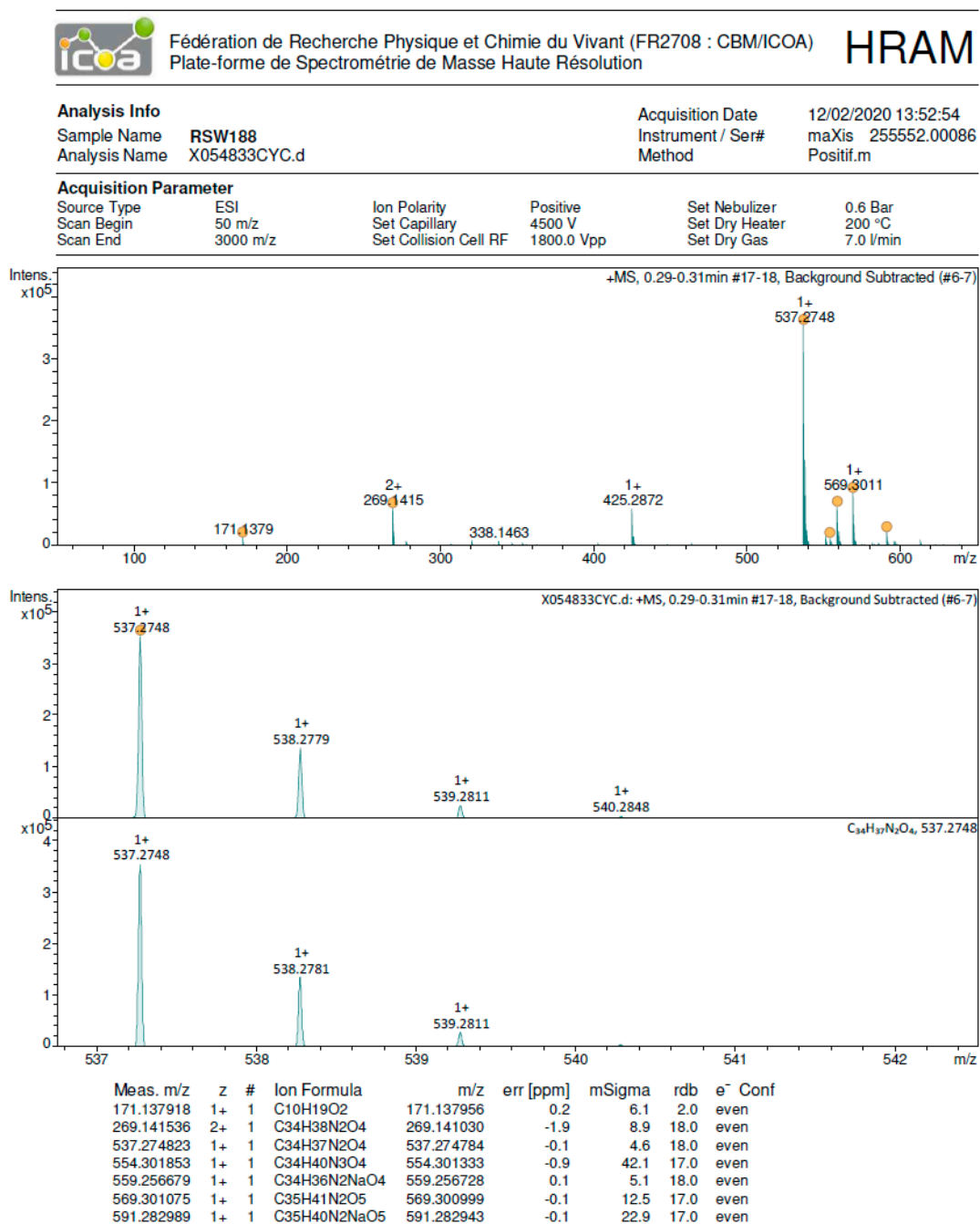


Figure S8. Mass spectra of Compound 4.

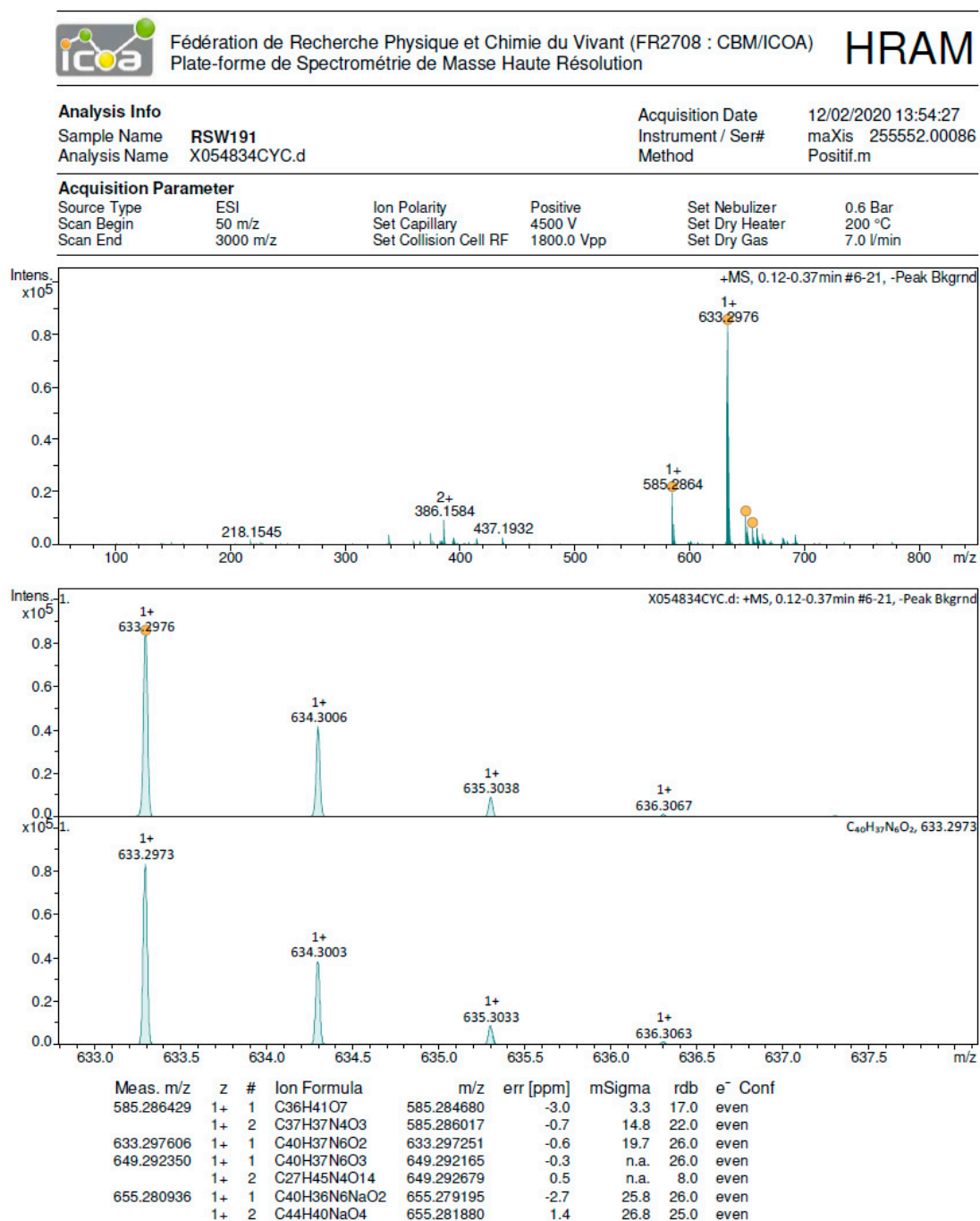
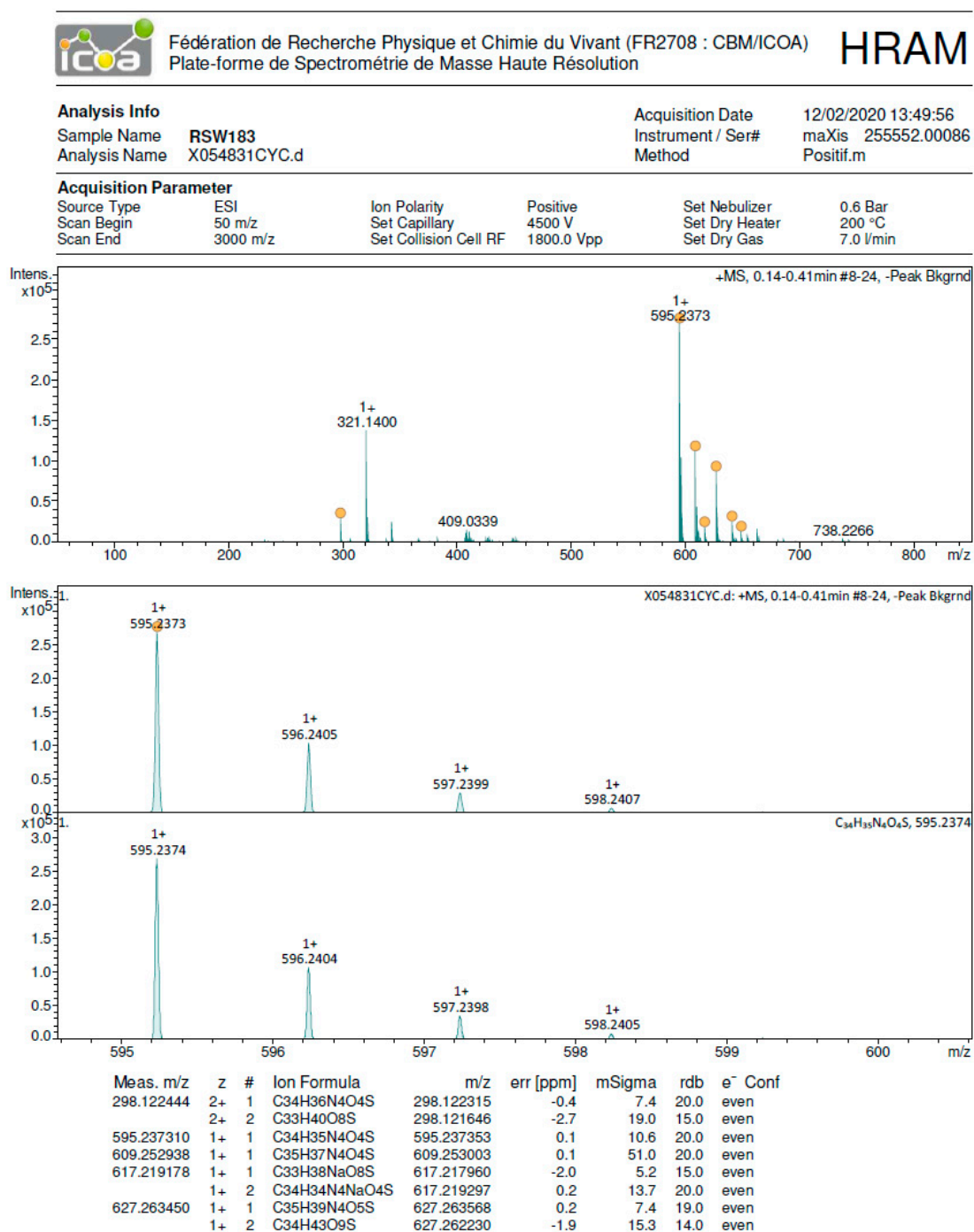


Figure S9. Mass spectra of Compound 5.



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Figure S10. Mass spectra of Compound 6.

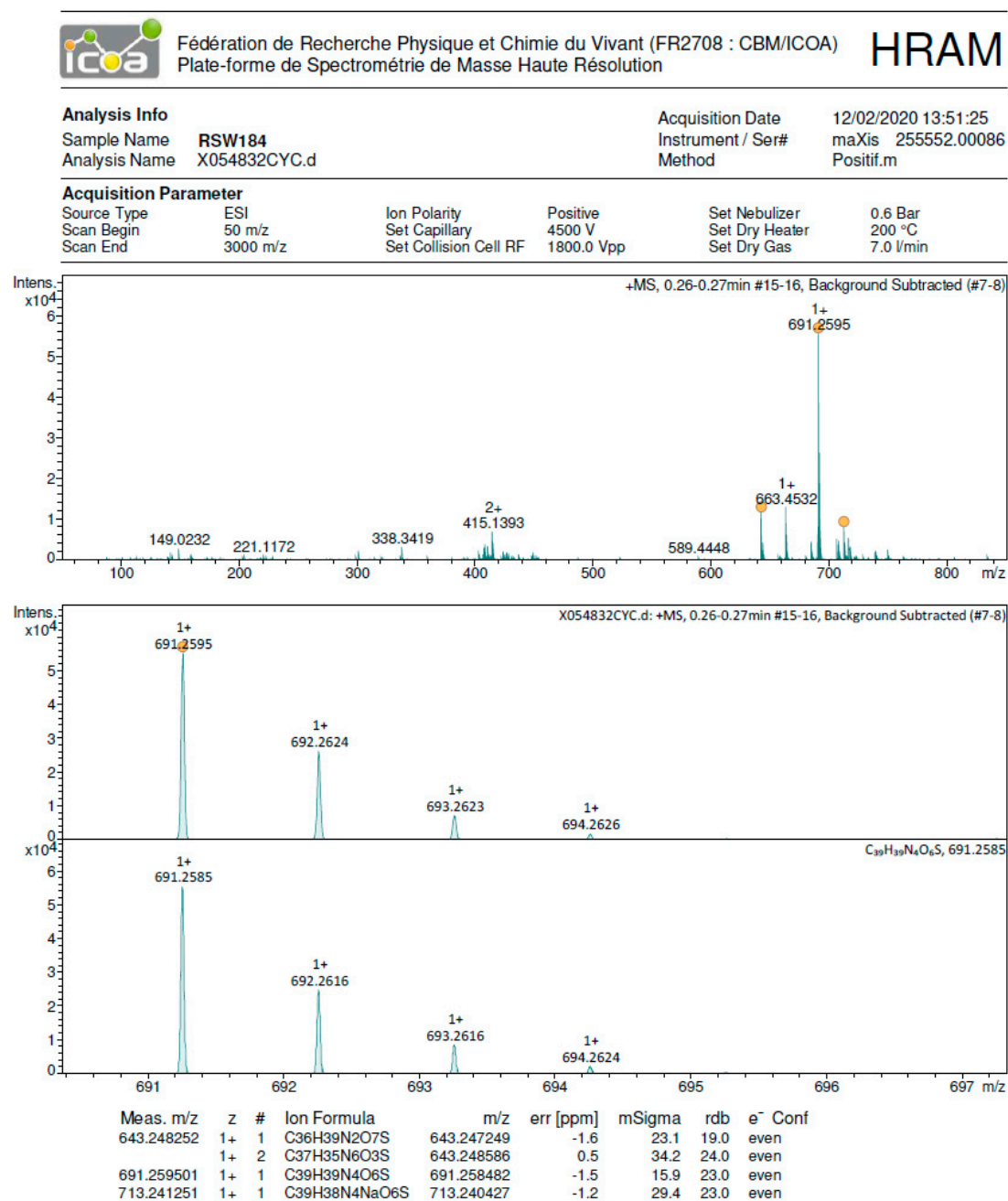


Figure S11. Mass spectra of Compound 7a.

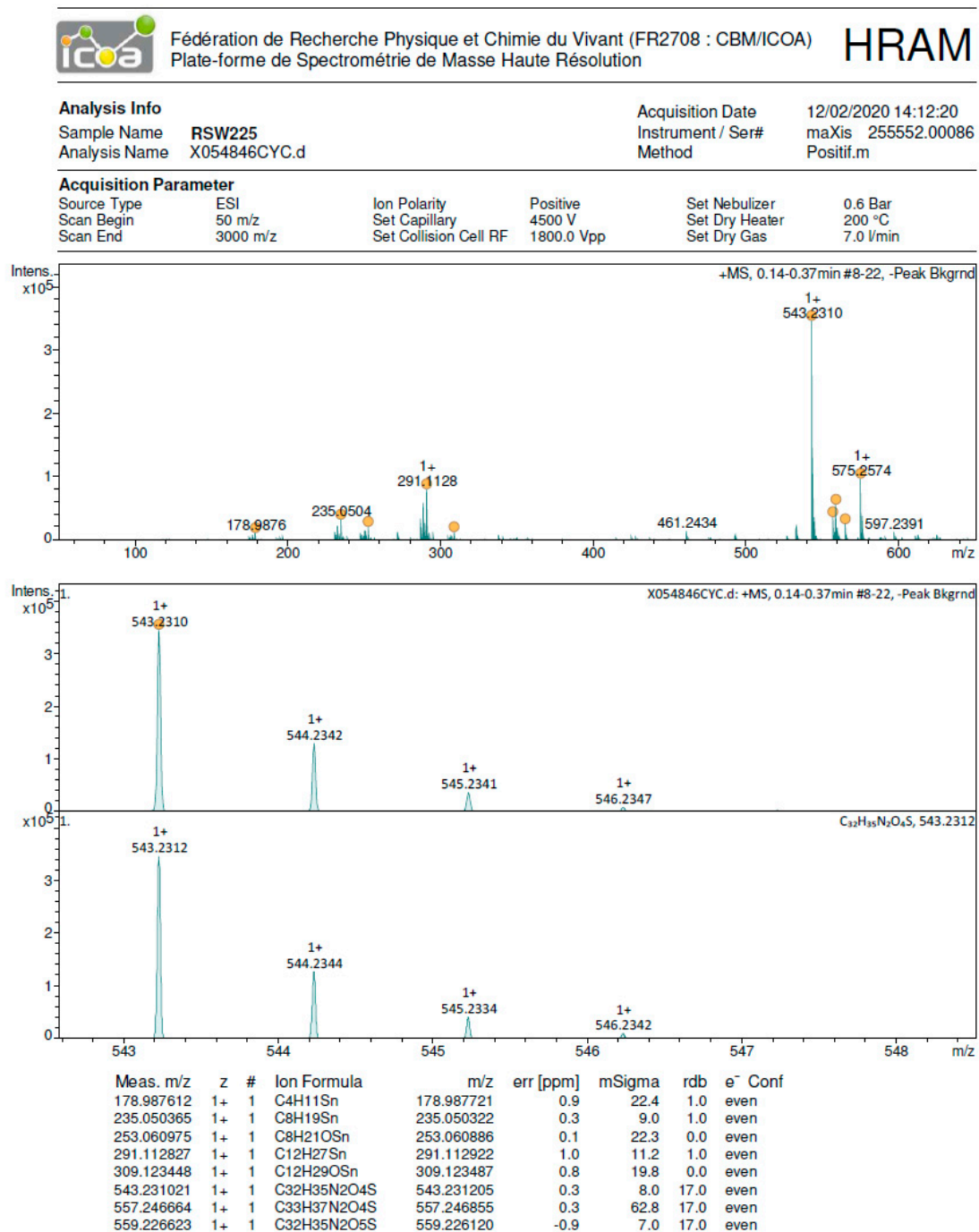


Figure S12. Mass spectra of Compound 8a.

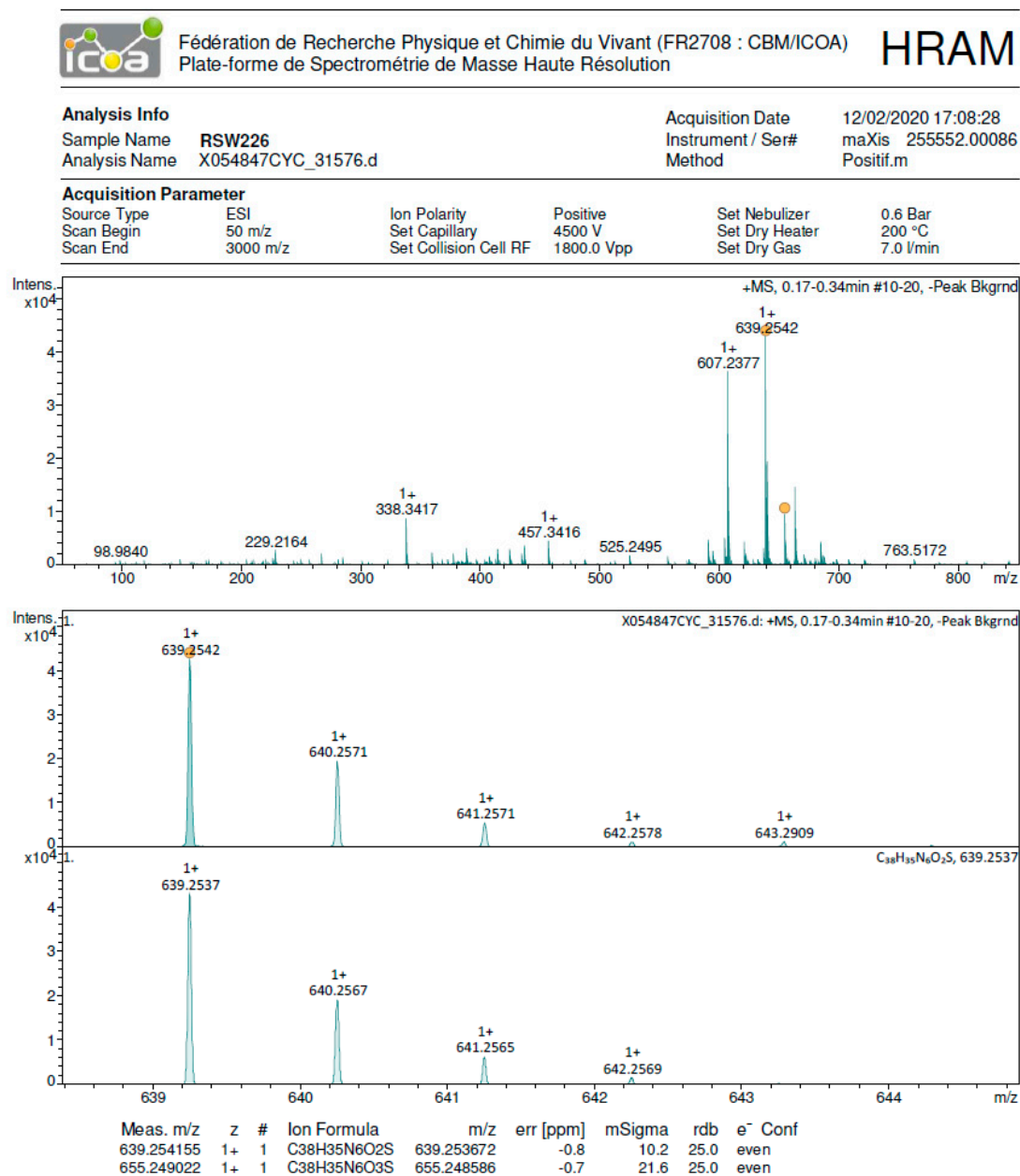


Figure S13. Mass spectra of Compound 7b.

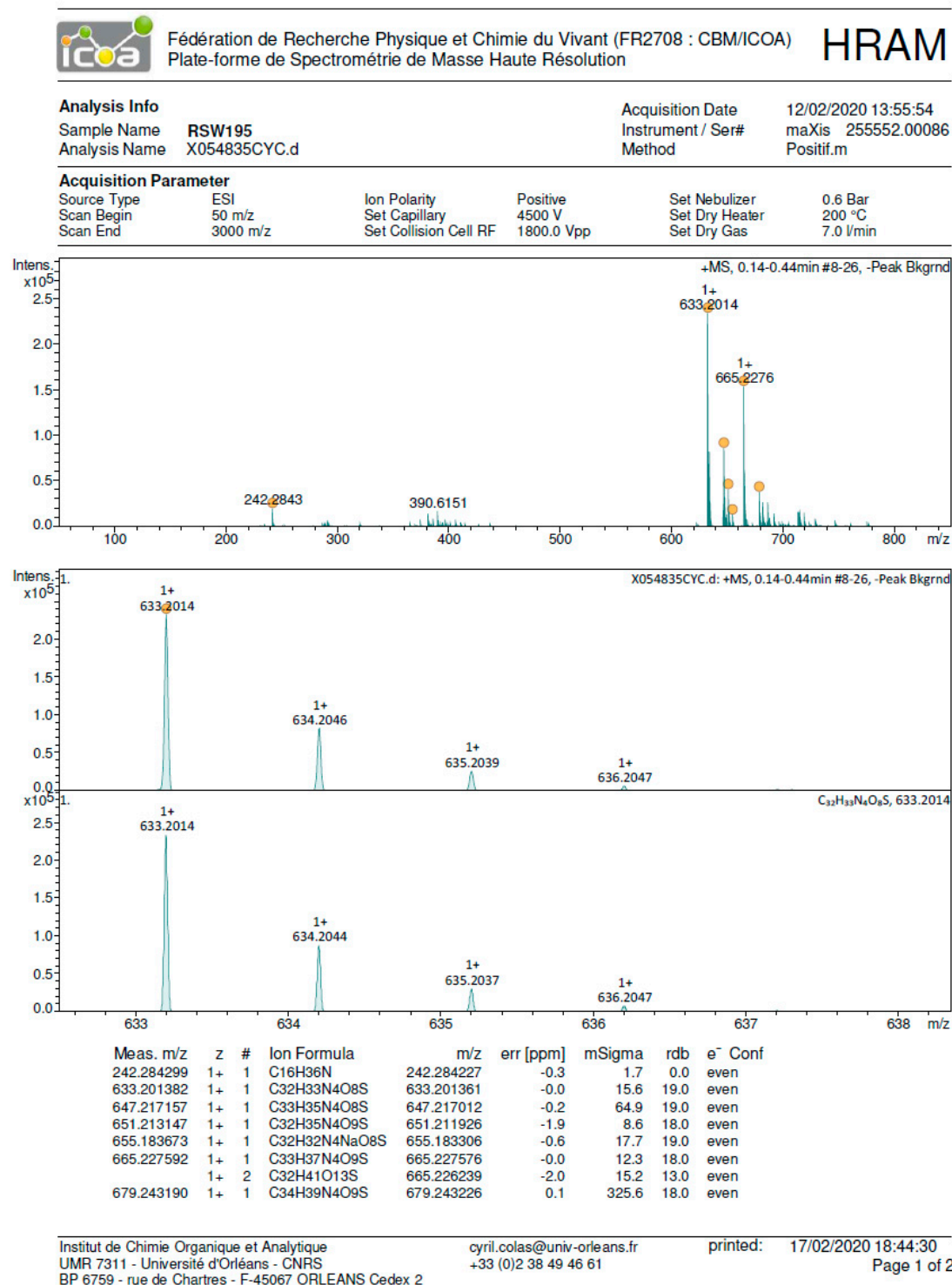


Figure S14. Mass spectra of Compound **8b**.

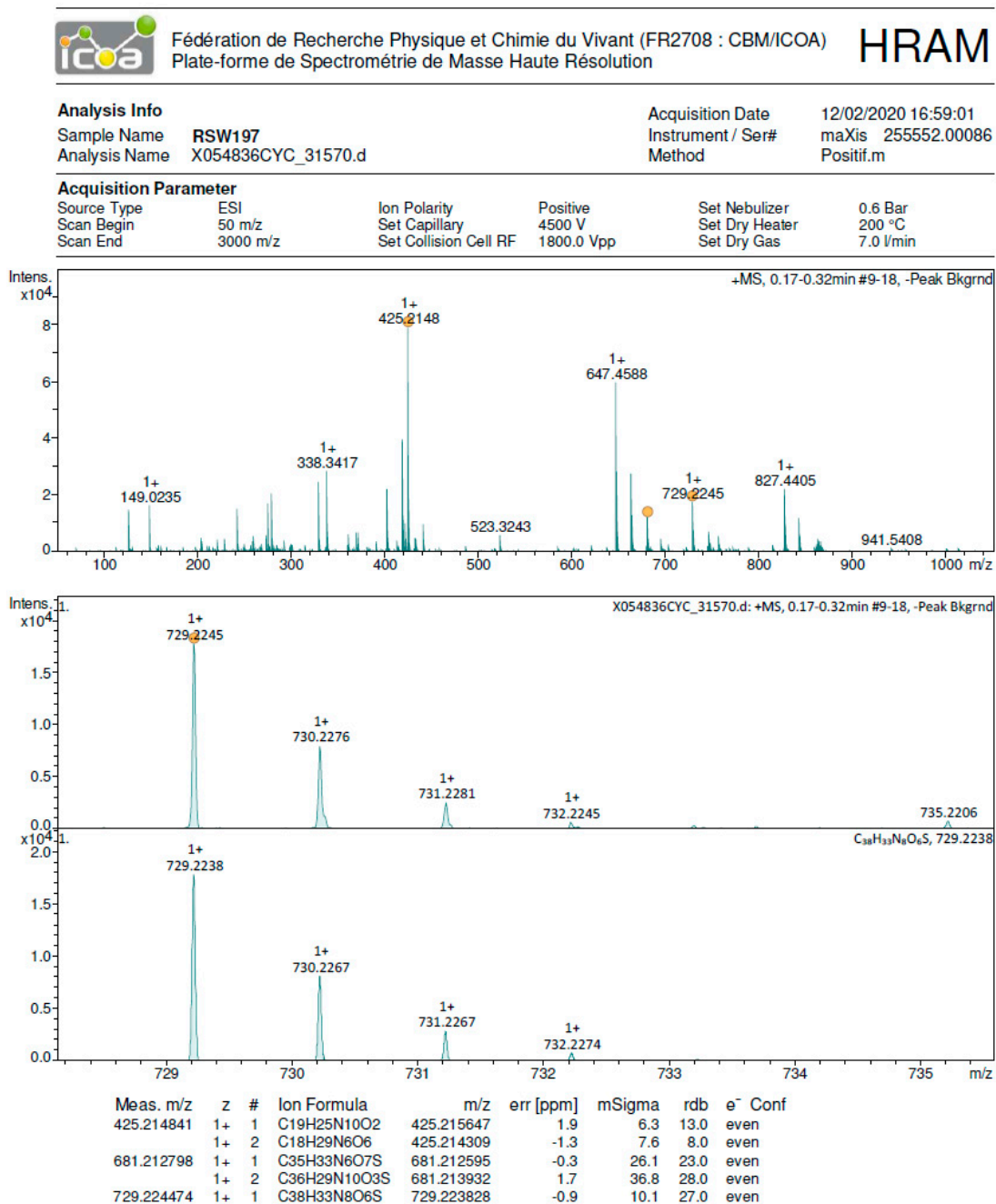


Figure S15. Mass spectra of Compound 18a.

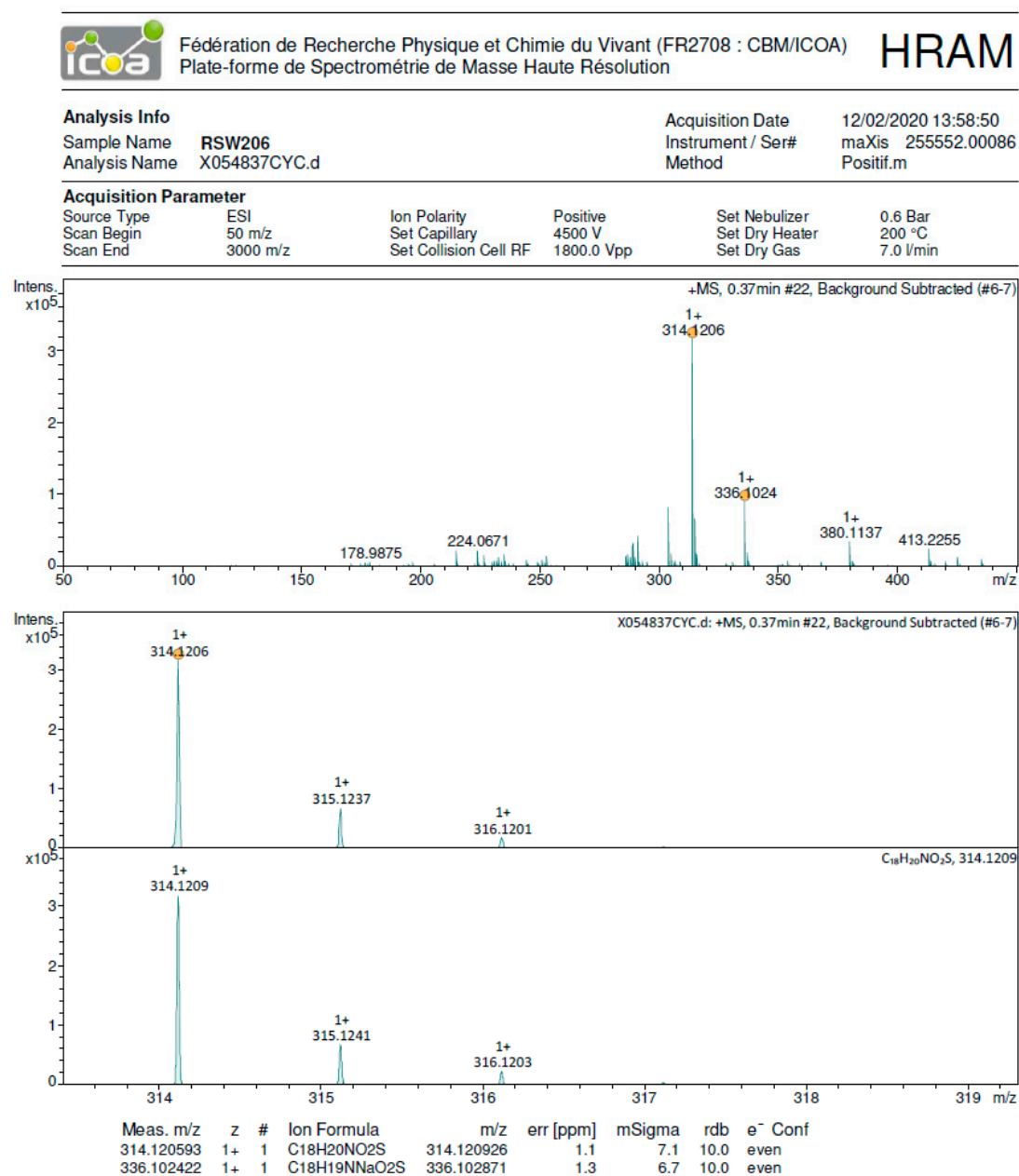


Figure S16. Mass spectra of Compound 19a.

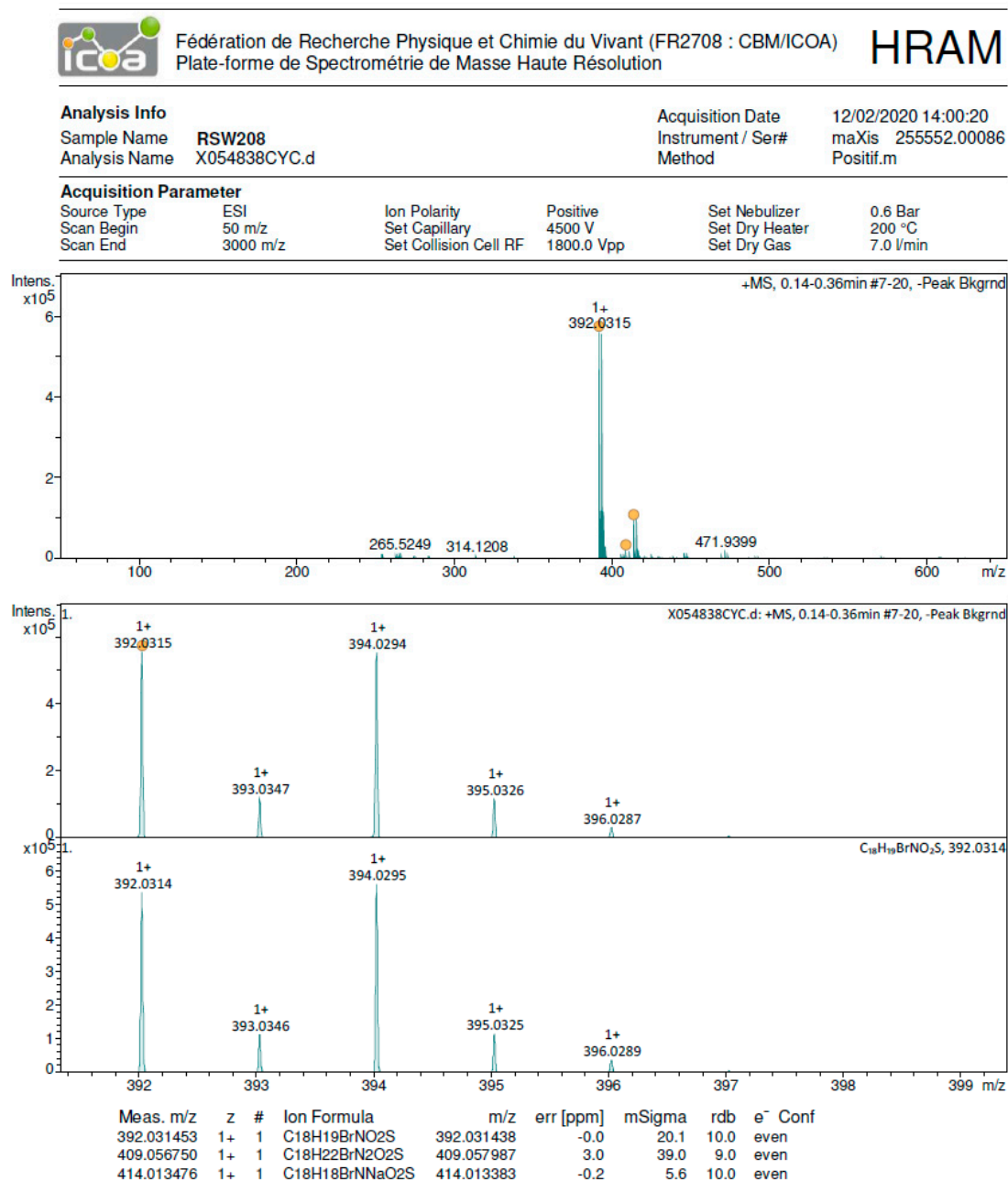
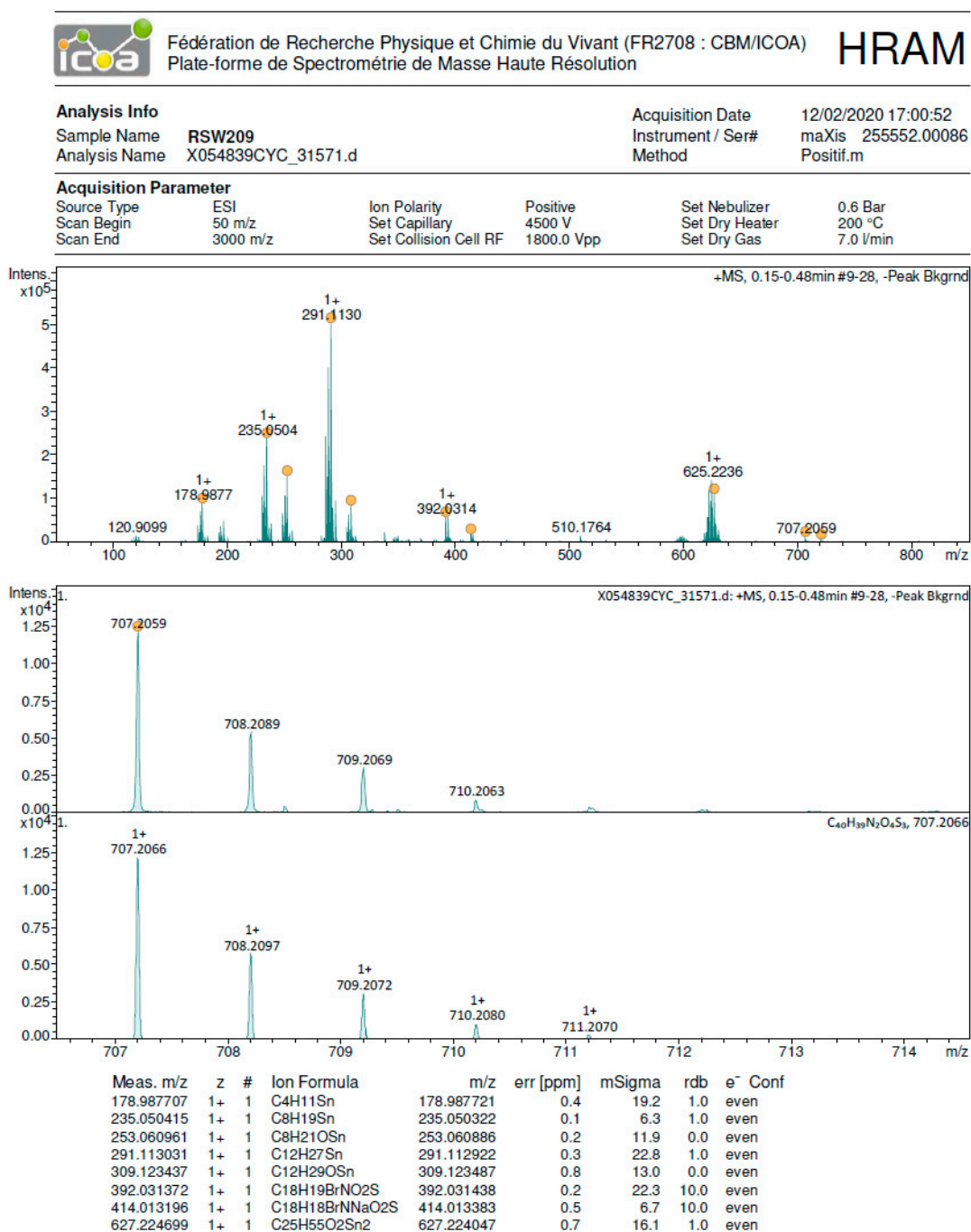


Figure S17. Mass spectra of Compound 9a.



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Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdb	e ⁻ Conf
707.205942	1+	1	C ₄₀ H ₃₉ N ₂ O ₄ S ₃	707.206647	1.0	17.2	23.0	even
721.222719	1+	1	C ₄₁ H ₄₁ N ₂ O ₄ S ₃	721.222297	-0.6	39.4	23.0	even

Figure S18. Mass spectra of Compound 10a.

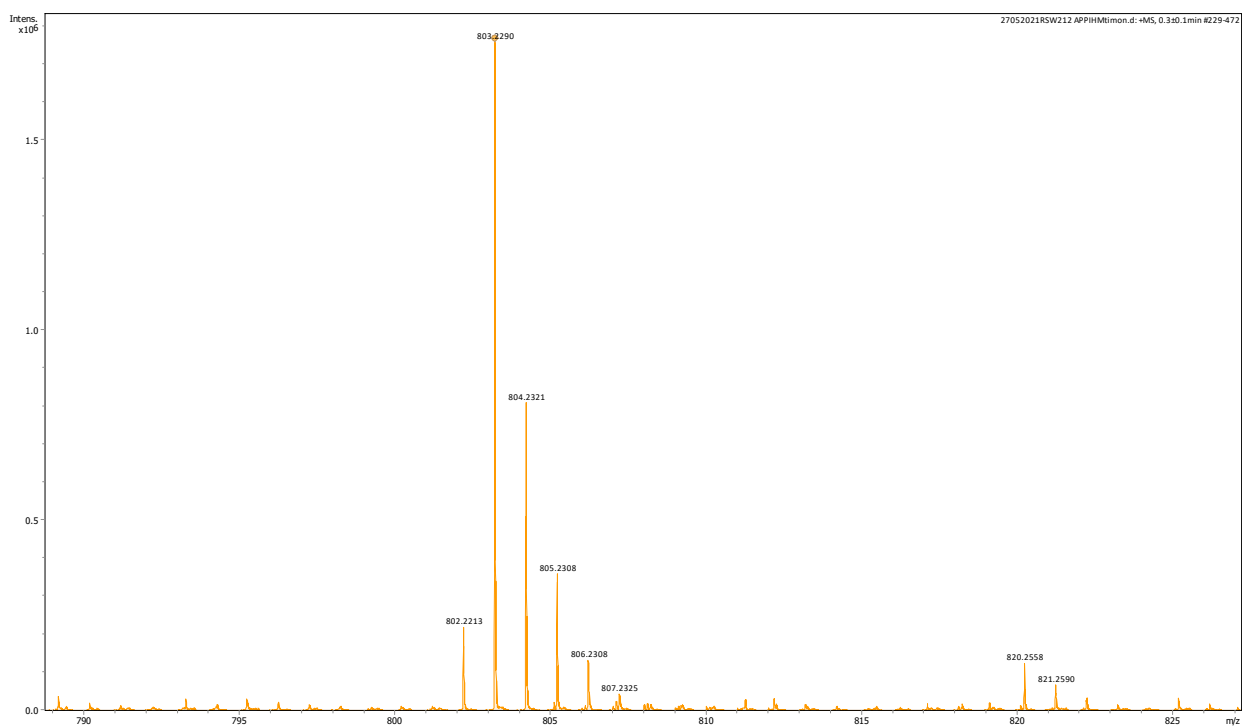
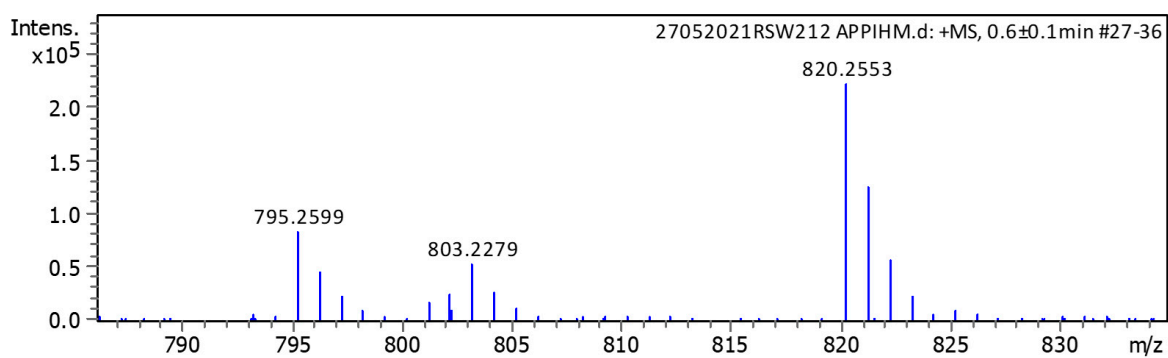
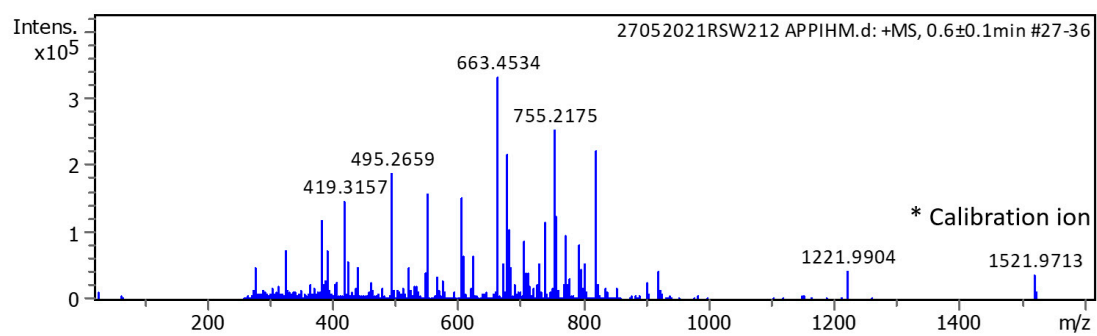


Figure S19. Mass spectra of Compound **18b**.

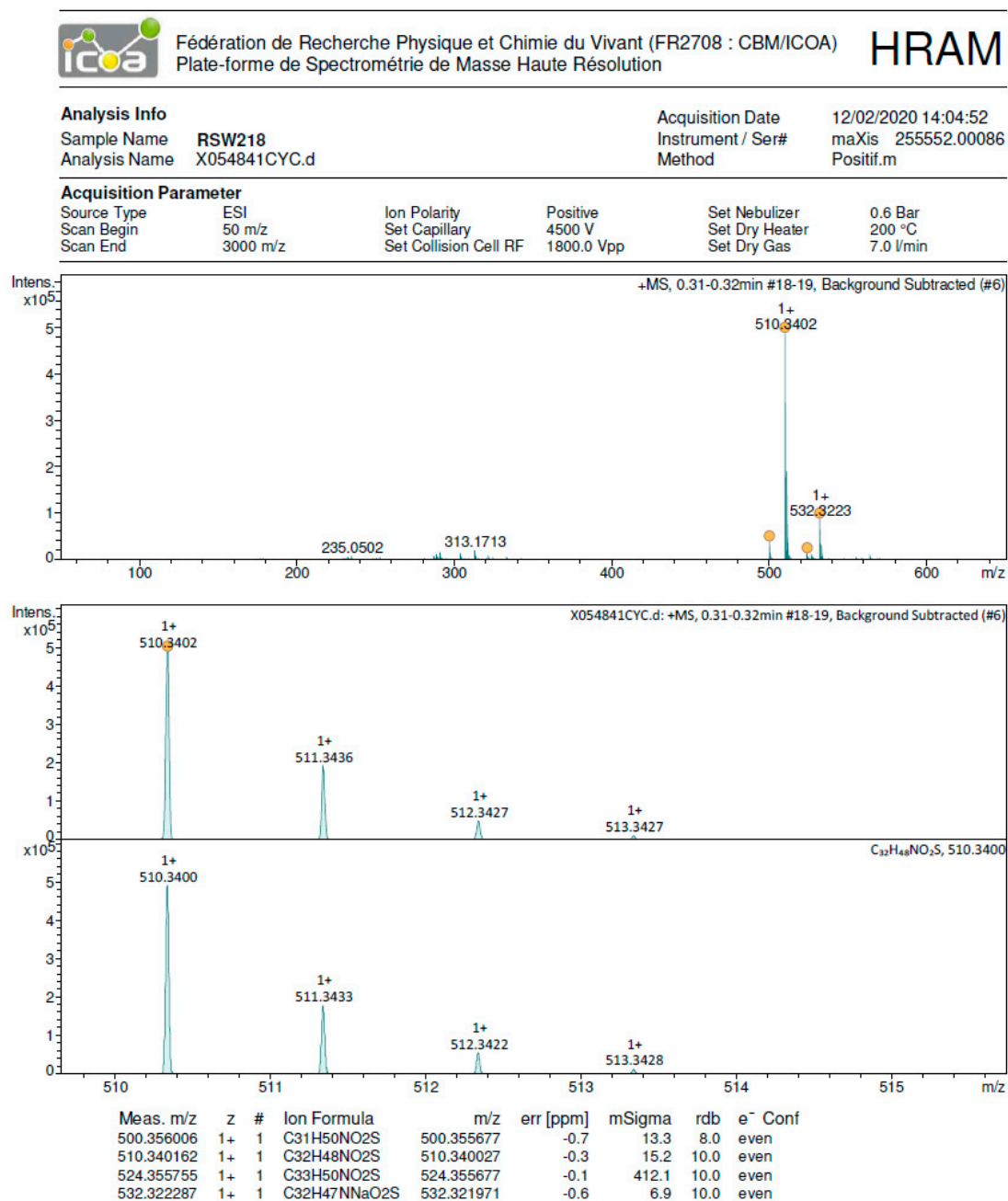


Figure S20. Mass spectra of Compound 19b.

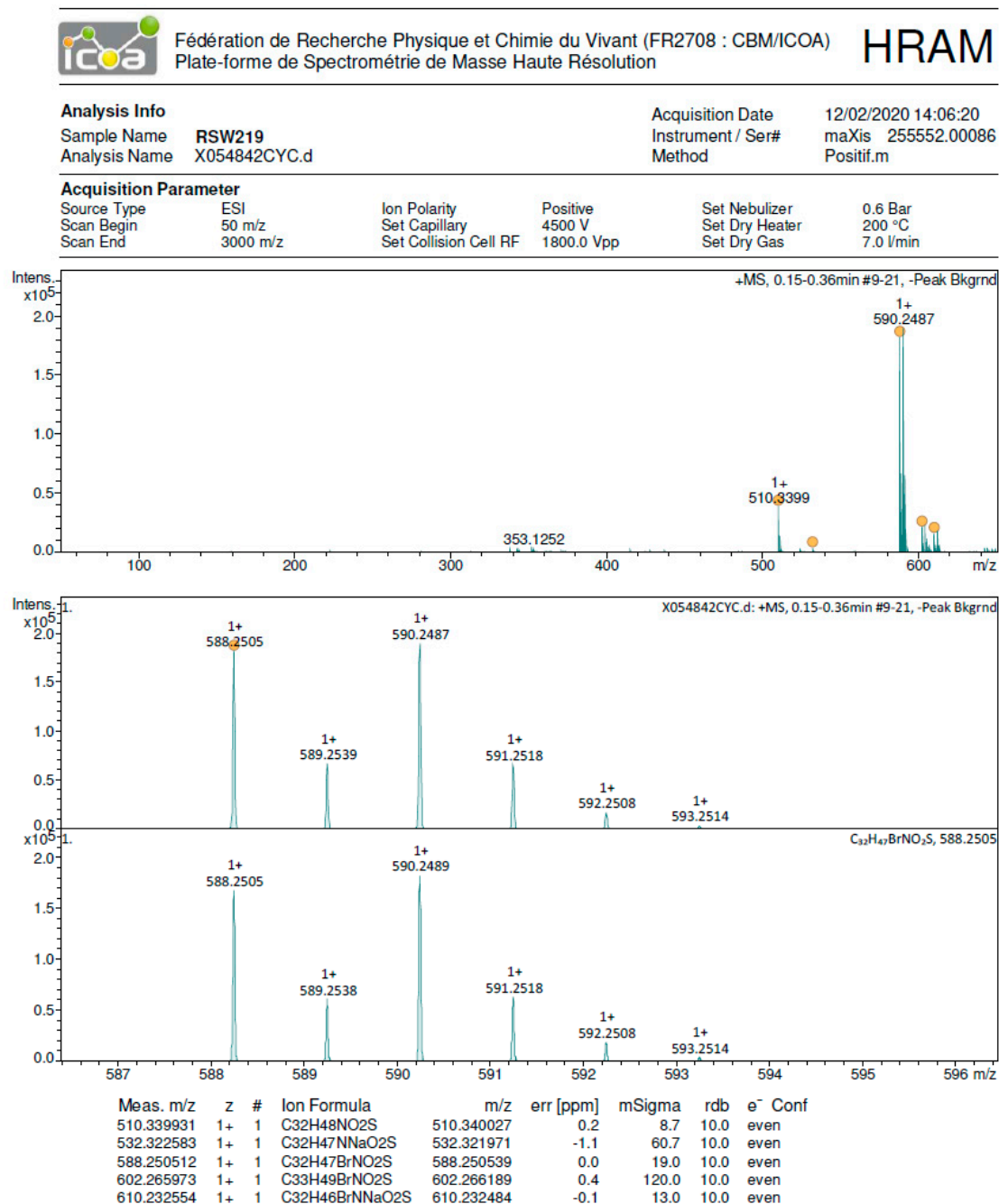


Figure S21. Mass spectra of Compound 9b.

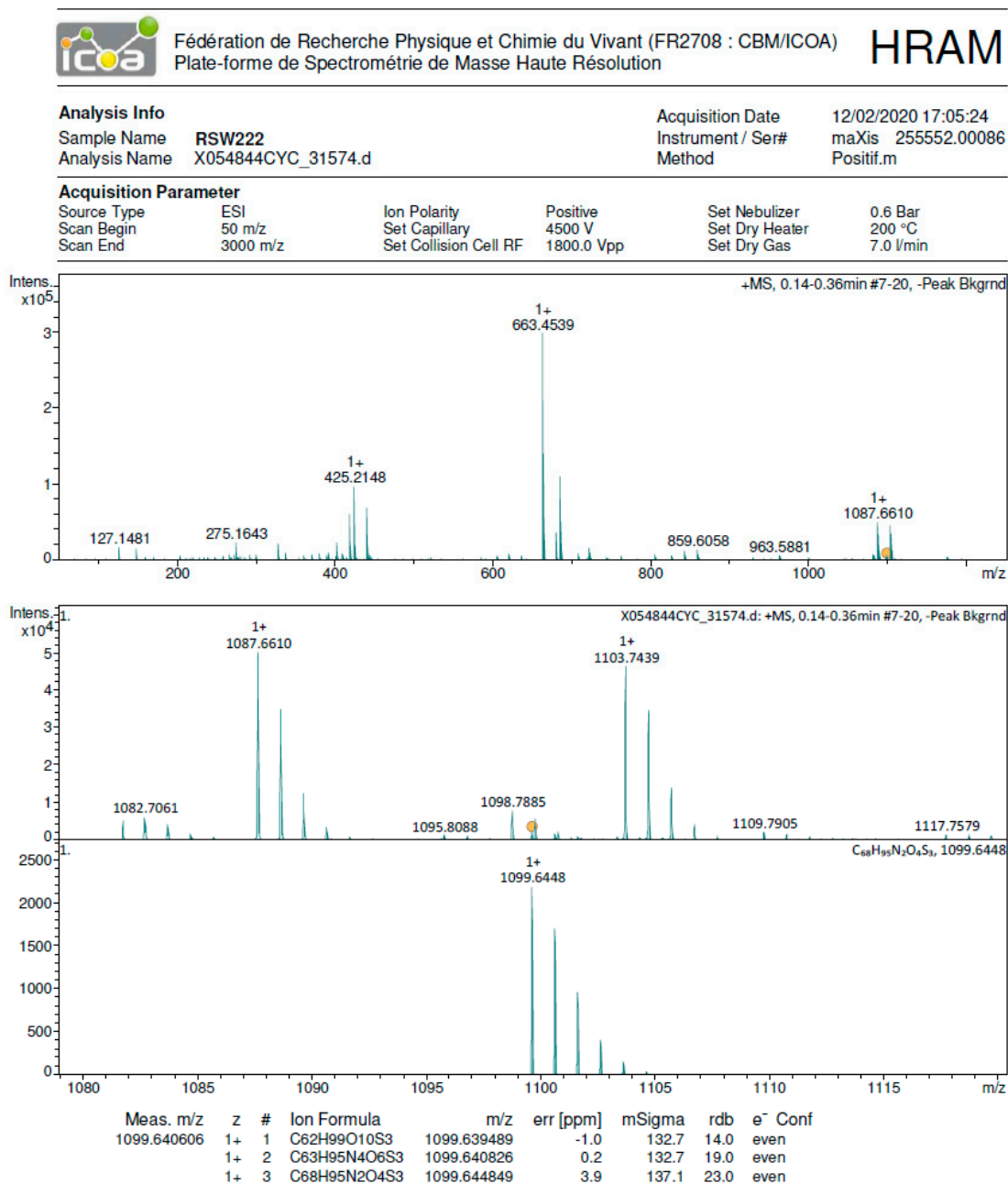
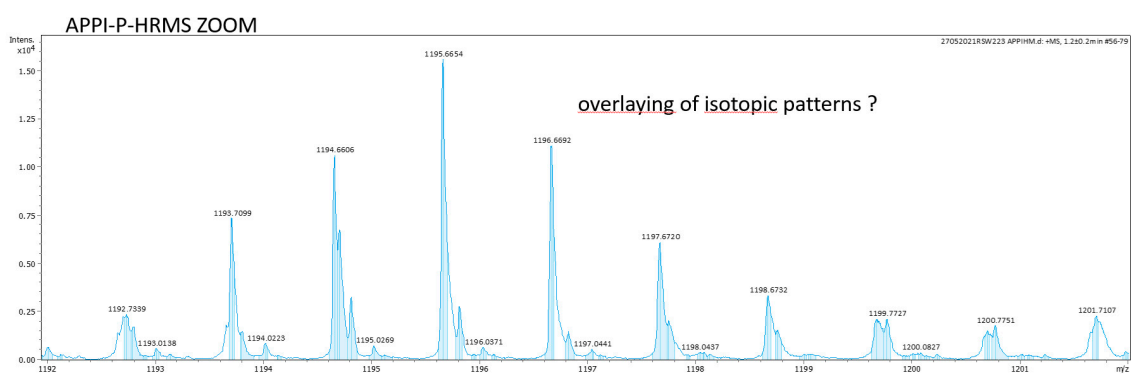
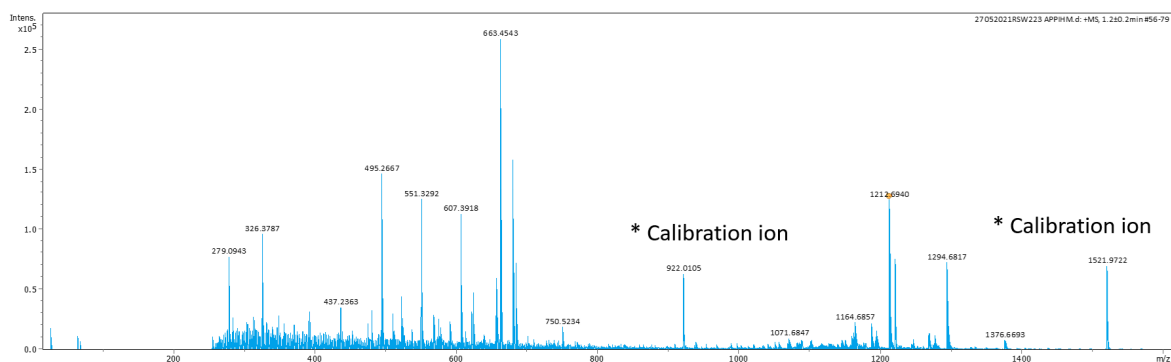


Figure S22. Mass spectra of Compound **10b**.



Meas. m/z	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻ Conf	N-Rule
1195.6653	C74H95N6O2S3	1195.6673	1.7	2	100.00	37.0	even	ok

9. ^1H and ^{13}C NMR spectra

NMR spectra of the obtained compounds are shown on the following pages.

