Electronic Supplementary Information

Carbazole/Fluorene based conjugated small molecules: Synthesis and comparative studies on the optical, thermal and electrochemical properties

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Contents

Experimental section

3,6-Dibromo-*N*-octyl carbazole (2):

To a mixture of N-octylcarbazole (5g, 18mmol) and acetic acid (15mL) was added bromine (1.9mL, 36.7mmol) dropwise (15 minutes). The mixture was stirred at room temperature for 3 hours. The precipitates formed were filtered and recrystallized from ethanol affording white crystals (6.7g, 85%).

Yield: 85%; M.p: 78-79°C; IR (υ/cm^{-1}, ATR): 3064 (sp^2 C-H stretch), 2965, 2835 (sp^3 C-H stretch), 1583 (Ar C=C), 1464 (CH_2 bend), 1376 (CH_3 bend), 1316 (C-N);^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.15 (d, J = 1.96 Hz, 2H, Ar-H), 7.56 (dd, J = 8.72, 1.96 Hz, 2H, Ar-H), 7.29 (d, J = 8.72 Hz, 2H, Ar-H), 4.24 (t, J= 7.20 Hz, 2H, N-CH_2), 1.85-1.81 (m, 2H, N-CH_2- CH_2), 1.32-1.24

(m, 10H), 0.87 (t, *J*= 6.76 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.2, 129.7, 123.3, 122.8, 118.2, 111.7, 55.4, 32.7, 30.5, 29.2, 28.8, 26.7, 22.6, 14.1; GC-MS (70eV): 437(439, 435 isotopic pattern) (M^+, 100%).

3-Bromo-9-octylcarbazole (3):

A solution of N-octylcarbazole (1g, 3.6mmol) in dry chloroform (15 mL) was stirred under nitrogen in a covered flask at 0°C. To this flask solution of NBS (0.64g, 3.6mmol) in dry $CHCl_3$ (25 mL) was added in two portions at 0°C and after complete addition flask was allowed to warm to room temperature and stirred for 6 hr under inert atmosphere. After completion of reaction the mixture was poured to water and extracted, concentrated in *vacuo* to give the brown oil that was purified by column chromatography on silica gel by eluting with hexane to afford a colourless oil (1.15g, 90%).

Yield: 90%; IR (υ/cm^{-1}, ATR): 3081 (sp^2 C-H stretch), 2961, 2815 (sp^3 C-H stretch), 1584 (Ar C=C), 1466 (CH_2 bend), 1375 (CH_3 bend), 1319 (C-N), 690 (C-Br);^1H NMR ($CDCl_3$, 400 MHz): δ 8.21 (d, *J*= 1.4 Hz, 1H, Ar-H), 8.00 (d, *J*= 7.71 Hz, 1H, Ar-H), 7.55-7.41 (m, 2H, Ar-H), 7.36-7.27 (m, 3H, Ar-H), 4.36 (t, *J*= 7.31 Hz, 2H, N-CH_2), 1.92-1.87 (m, 2H, N-CH_2-CH_2), 1.41-1.25 (m, 10H), 0.89 (t, *J*= 6.91 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 139.2, 128.6, 126.3, 124.8, 123.3, 121.7, 120.6, 119.8, 115.4, 110.2, 109.5, 51.3, 31.8, 29.6, 29.0, 28.2, 27.4, 22.6, 14.3.

9-(6-Bromo-9-octyl-9*H*-carbazol-3-yl)-9*H*-carbazole (4):

It was prepared according to above reported method using N-Octyl-3,6-dibromocarbazole (7.55g 17.2 mmol), carbazole (2.2g, 13.2 mmol), cuprous iodide (0.27g, 1.42 mmol), 18-crown-6 (0.13g, 0.49 mmol), K_2CO_3 (3.4g, 24.6 mmol), *o*-dichloro benzene (10mL). Crude was purified by column chromatography using (Hexane/DCM 7:1) to obtain compound as white solid (4.9g, 71%).

Yield: 71%; Mp:141-143°C; R_f: 0.39; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.30 (d, *J*= 1.8 Hz, 1 H, Ar-H), 8.21 (d, *J*= 2.0 Hz, 1 H, ArH), 8.12 (d, *J*= 7.8 Hz, 2H, Ar-H), 7.84 (d, *J*= 8.1 Hz, 1H, Ar-H), 7.72–7.62 (m, 3 H, Ar-H), 7.44–7.36 (m, 4 H, Ar-H), 7.29 (dt, J_1=1.4 Hz, J_2=7.9 Hz, 2H, Ar-H), 4.25 (t, *J*= 7.2 Hz, 2H, N-CH_2), 1.85–1.80 (m, 2 H), 1.71–1.24 (m, 10 H), 0.87 (t, *J*= 7.1 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.9, 139.7, 133.1, 129.3, 125.9, 123.4, 122.6, 121.7, 120.2, 119.6, 117.4, 112.0, 111.0, 111.8, 110.5, 110.0, 109.7, 43.7, 31.8, 30.7, 29.3, 27.4, 22.6, 14.1; MS (m/z, APCI): 523.2 (M^+), 525.1 (M+2).

2,7-dibromo-9,9-dioctyl-9*H*-fluorene (7):

2,7-Dibromofluorene (3g, 9.2 mmol) was dissolved in DMSO (15 mL). To this 1-bromoctane (3.7g, 19.1 mmol), KI (0.17g, 1.0 mmol) was added and mixture was degaseed and filled with nitrogen thrice. Then powdered KOH (2.3g, 41mmol) was added at once and again degassing and refilling with nitrogen was carried out. The mixture was stirred under inert atmosphere for 6 hours, poured into water and precipitates were collected by filtration and recrystallized from ethanol to give pale yellow needle like crystals (4.1g, 81%).

Yield: 81%; R_f: 0.81; Mp: 51-51.5°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, *J*= 7.76, 1.1 Hz, 2H, Ar-H), 7.47 (d, *J*= 1.8 Hz, 2H, Ar-H), 7.44 (d, *J*= 1.1 Hz, 2H, Ar-H), 1.94-1.89 (m, 4H, C-CH_2), 1.25-1.05 (m, 20H), 0.81 (t, *J*= 7.24 Hz, 6H, CH_3), 0.56 (quint, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.2, 139.8, 131.2, 126.2, 122.3, 121.1, 46.4, 41.8, 31.7, 29.6, 29.0, 23.9, 22.8, 14.1; Anal for $C_{29}H_{40}Br_2$: Calcd (%) C= 63.51, H= 7.35, Found C= 63.41, H= 7.33.

2-bromo-9,9-dioctyl-9*H*-fluorene (8):

The compound was synthesized according to above reported method for compound (**8**) using 2-Bromofluorene (1.0g, 4.07 mmol), DMSO (10 mL), 1-bromoctane (1.8g, 9.3 mmol), KI (0.07g, 0.4 mmol), KOH (1.2g, 20 mmol) upon overnight stirring at room temperature. Reaction mixture was diluted with ethyl acetate and organic layer was washed with water, separated and concentrated in *vacuo*. Crude product was purified by column chromatography using hexane as eluent to afford the light yellow oil.

Yield: 88%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69-7.68 (m, 1H, Ar-H), 7.57 (dd, *J*= 7.88, 1.4 Hz, 1H, Ar-H), 7.49-7.46 (m, 2H, Ar-H), 7.35-7.33 (m, 3H, Ar-H), 1.98-1.91 (m, 4H, C-CH_2), 1.27-1.10 (m, 20H), 0.91 (t, *J*= 7.34 Hz, 6H, CH_3), 0.79 (quint, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 148.2, 141.6, 140.3, 135.5, 131.7, 130.2, 128.7, 127.9, 126.4, 122.1, 44.1, 43.3, 31.8, 30. 6, 29.9, 29.2, 24.2, 22.6, 14.2; Anal for $C_{29}H_{41}Br$: Calcd (%) C= 74.18, H= 8.80, Found C= 74.27, H= 8.79.

9-(7-Bromo-9,9-dioctylfluoren-2-yl)-9*H*-carbazole (11):

A mixture of 2,7-dibromo-9,9-dioctylfluorene (10g, 18.2 mmol), carbazole (2.6g, 15.5 mmol), cuprous iodide (0.3g, 1.57 mmol), 18-crown-6 (0.14g, 0.53 mmol), K_2CO_3 (4.3g, 31 mmol) was suspended in *o*-dichloro benzene (10mL) and heated at 180 °C for four days under nitrogen atmosphere. Upon completion of reaction, the reaction mixture was cooled and diluted with dichloromethane and filtered through a short silica plug to remove CuI and concentrated in *vacuo*

to give orange brown oil. The *o*-dichloro benzene was removed upon vacuum distillation and the resulting brown mixture was purified by column chromatography using (Hexane/DCM 6:1) to afford a colourless oil (5.6g, 57%).

Yield: 57%; R_f: 0.46; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18 (2H, dt, *J*= 1.9 Hz, 7.7 Hz), 7.88 (dd, *J*= 0.44 Hz, 7.96 Hz, 1H, Ar-H), 7.64 (d, *J*= 8.5 Hz, 1H, Ar-H), 7.56-7.52 (m, 4H, Ar-H), 7.44–7.42 (m, 4 H), 7.33–7.30 (m, 2H), 2.00-1.96 (m, 4H), 1.21–1.11 (m, 20H), 0.83 (t, *J*= 7.10 Hz, 6H, CH_3), 0.75-0.73 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 153.2.9, 152.5, 141.0, 139.3, 139.0, 130.3, 129.7, 126.4, 126.1, 125.9, 123.4, 121.8, 129.2, 120.9, 120.3, 119.9, 109.7, 55.6, 40.2, 31.8, 29.9, 29.2, 23.9, 22.6, 14.1; MS (m/z, APCI): 634.3 (M^+), 636.3 (M+2).

General procedure for synthesis of boronic acid:

The synthesized brominated compounds (**2, 3, 7, 8**) were dissolved in dry THF (30 mL) in an oven dried 100 mL flask and cooled to -78°C. To this n-BuLi was added dropwise and stirred for 1 hour. Afterward Tri-isopropyl borate was added and reaction was stirred overnight at room temperature, quenched with 2 M HCl (20 mL), further stirred for one hour and extracted with diethyl ether. Organic layers were separated, dried over anhydrous $MgSO_4$, concentrated and vacuum dried for 01 hour in vacuum oven at room temperature under reduced pressure used without further purification.

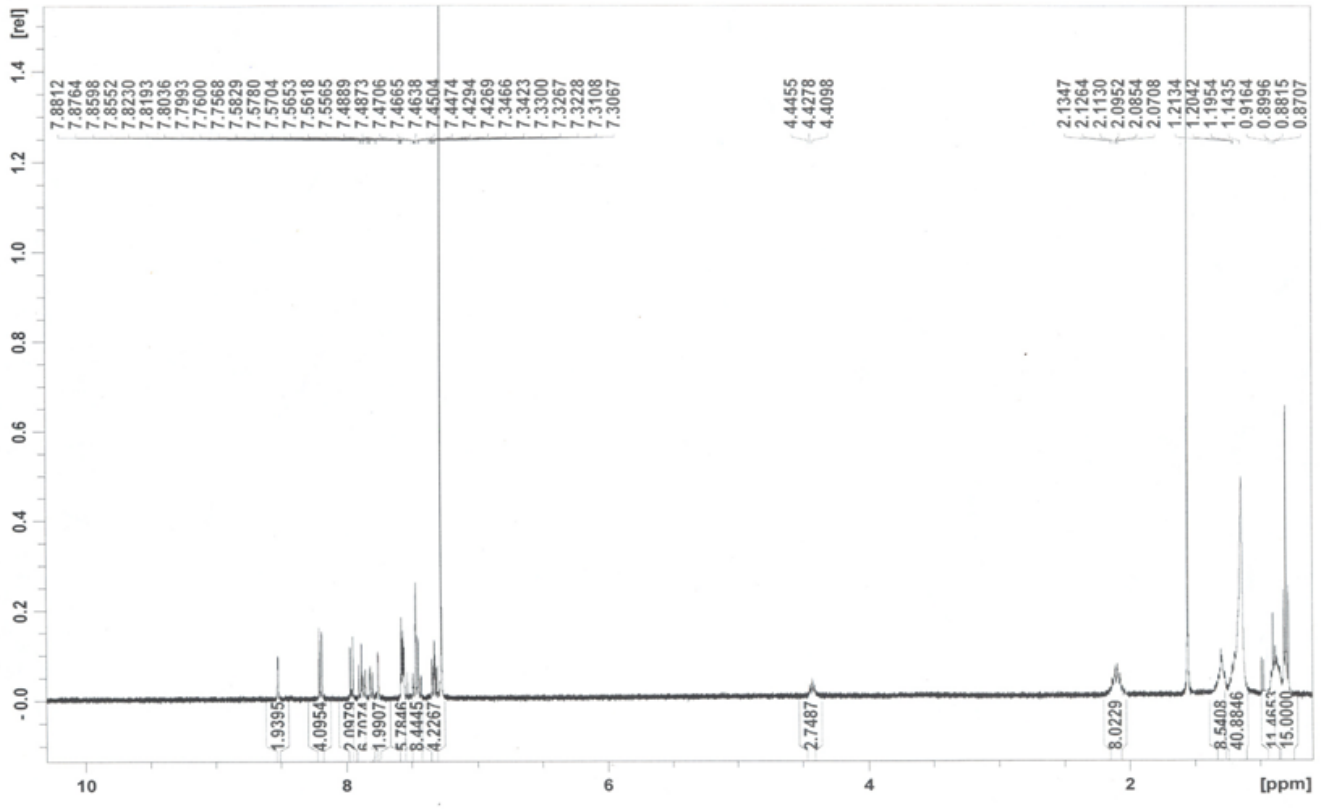

Fig. S1 ^{1}H-NMR spectrum of **CFT**

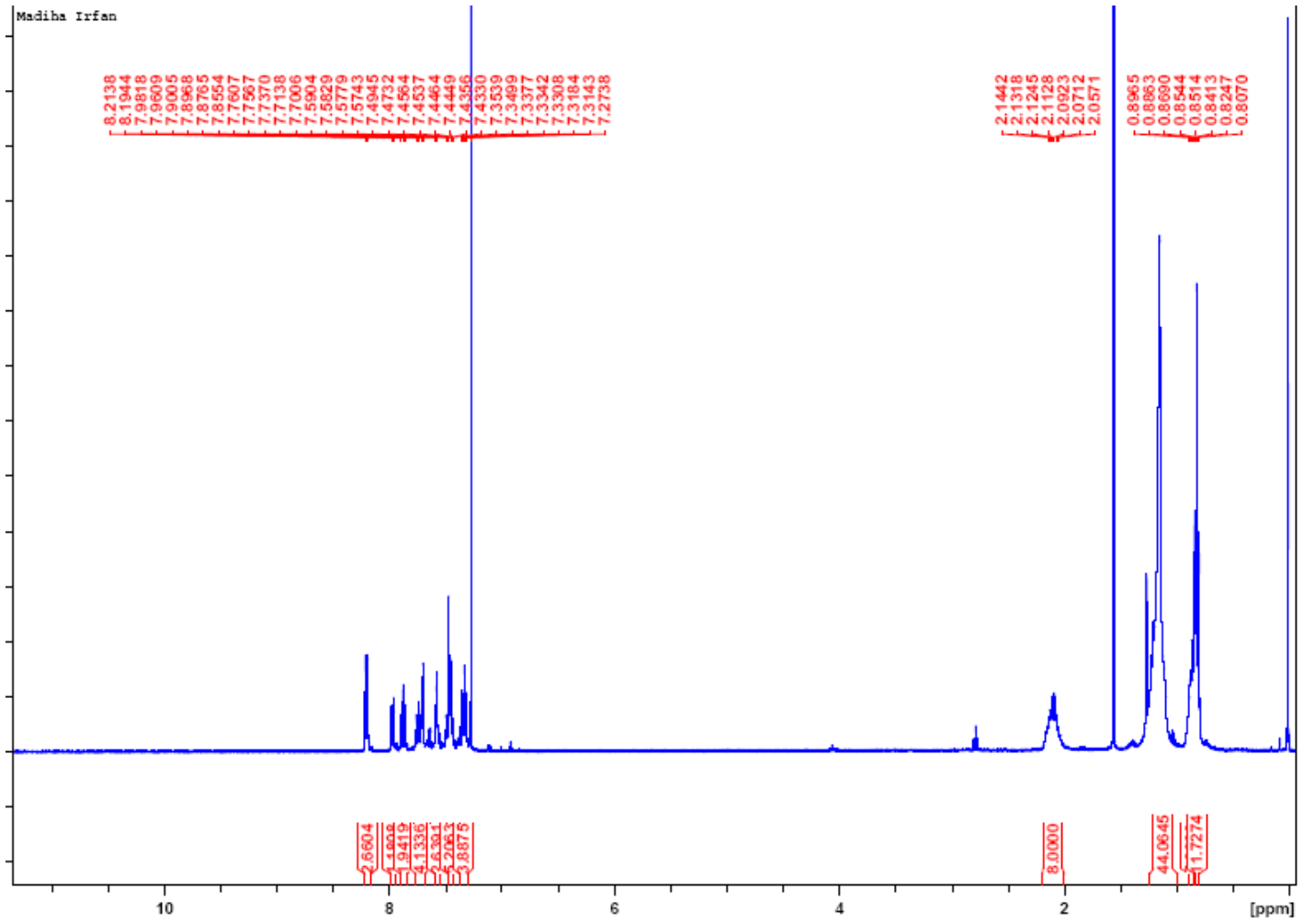

Fig. S2 ^{1}H-NMR spectrum of **CFM**

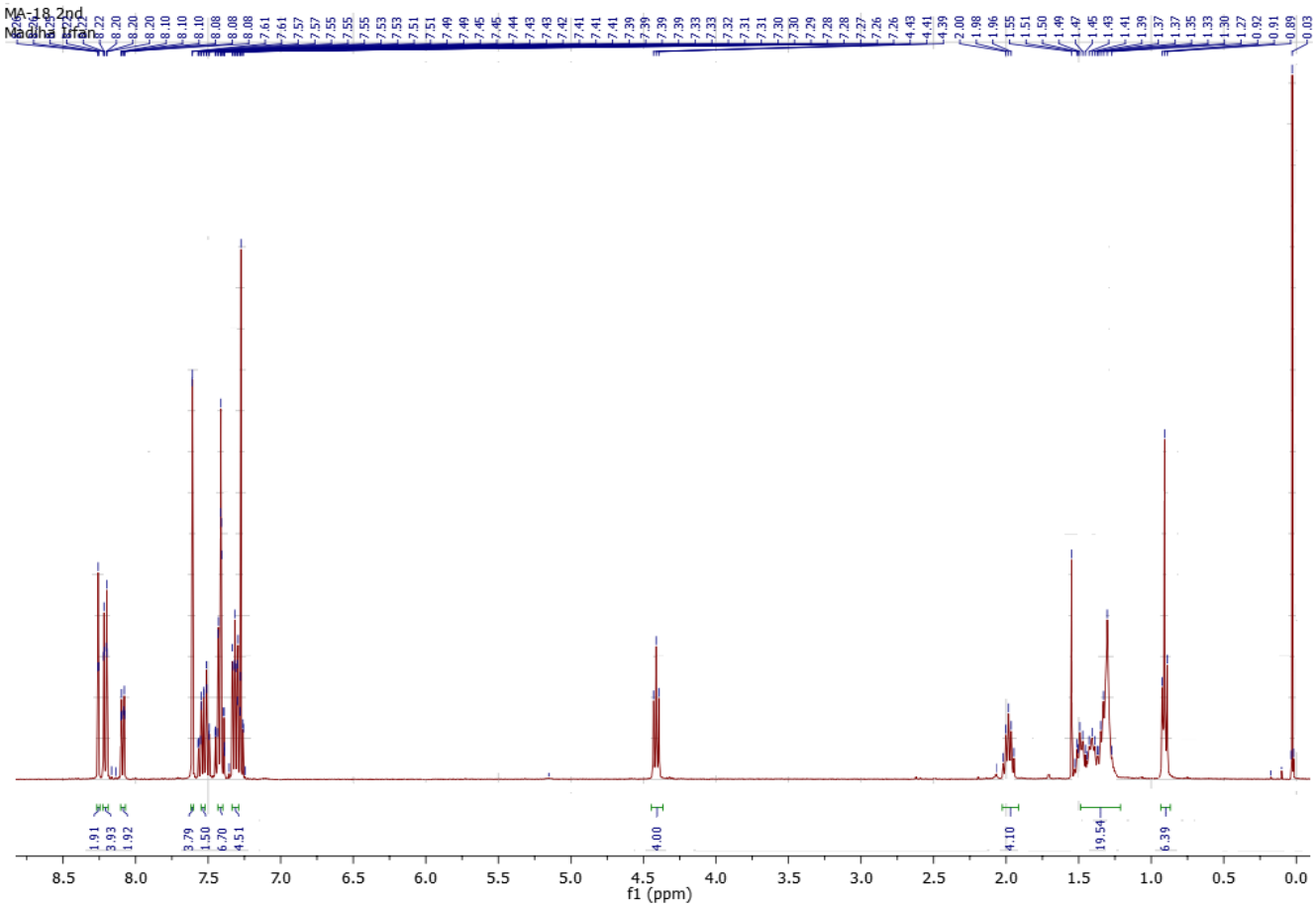

Fig. S3 ^{1}HNMR spectrum of **CCT**

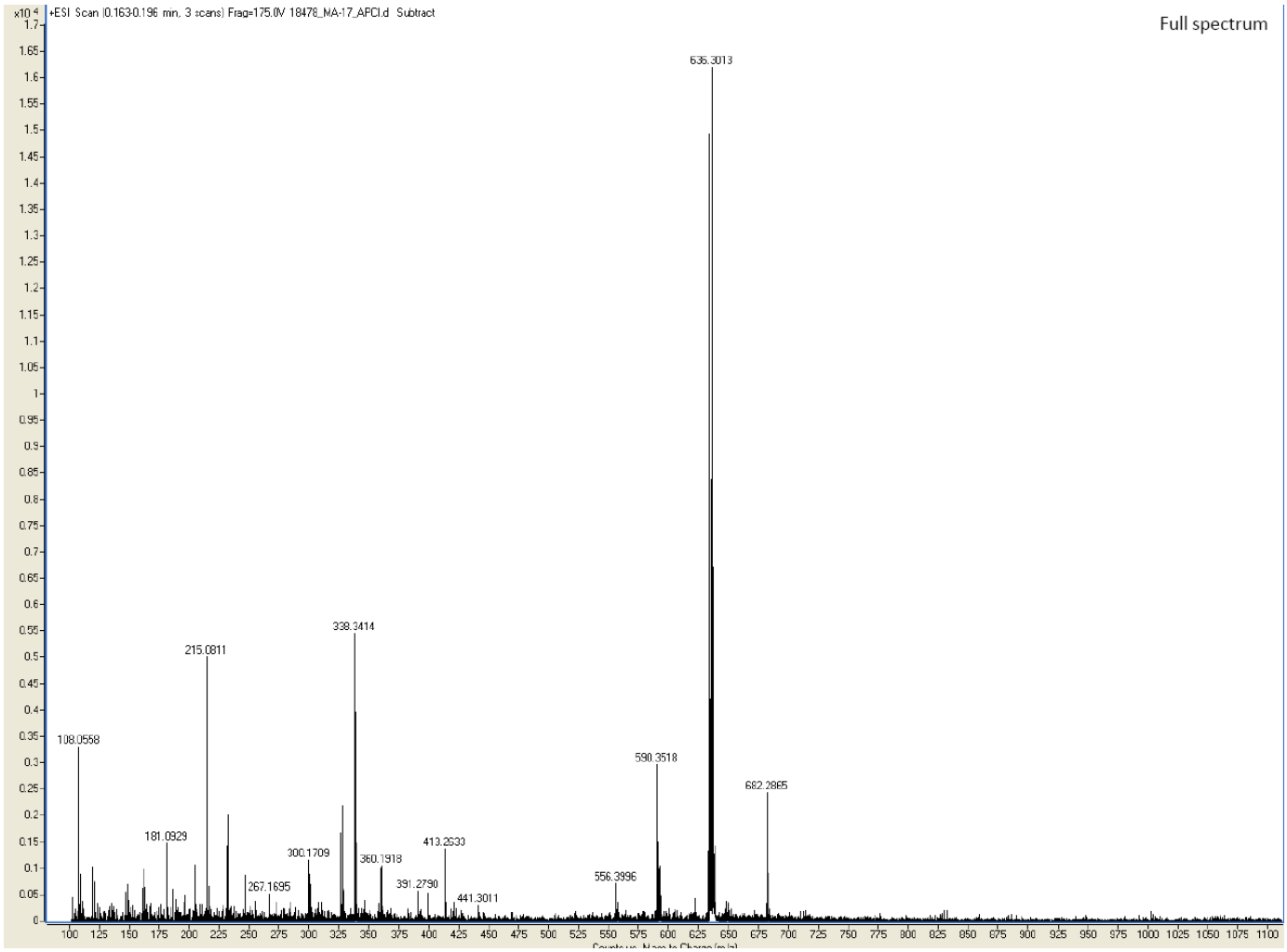

Fig. S4 APCI-MS of bromo fluorene derivative (**13**)

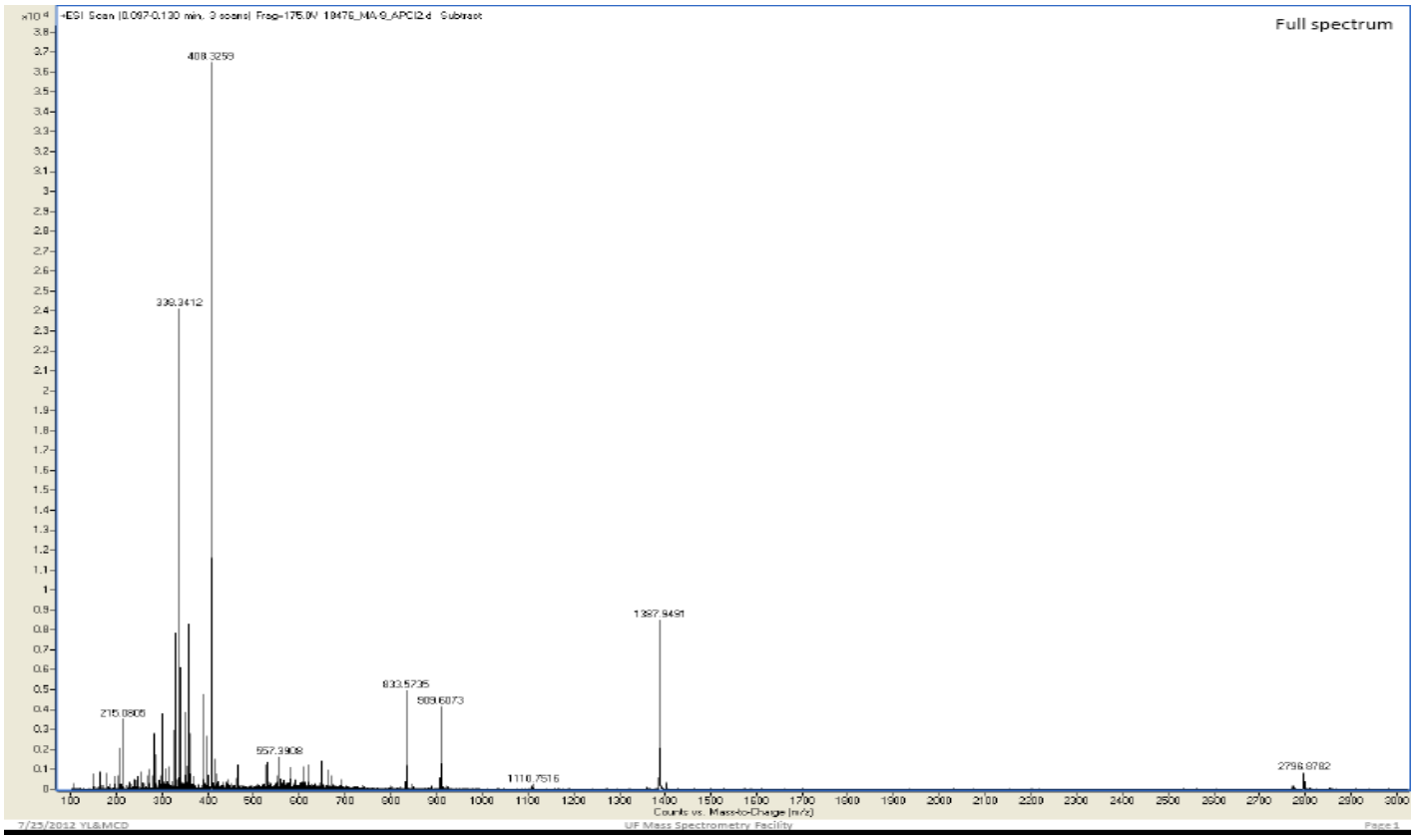

Fig. S5APCI-MS of **CFT**

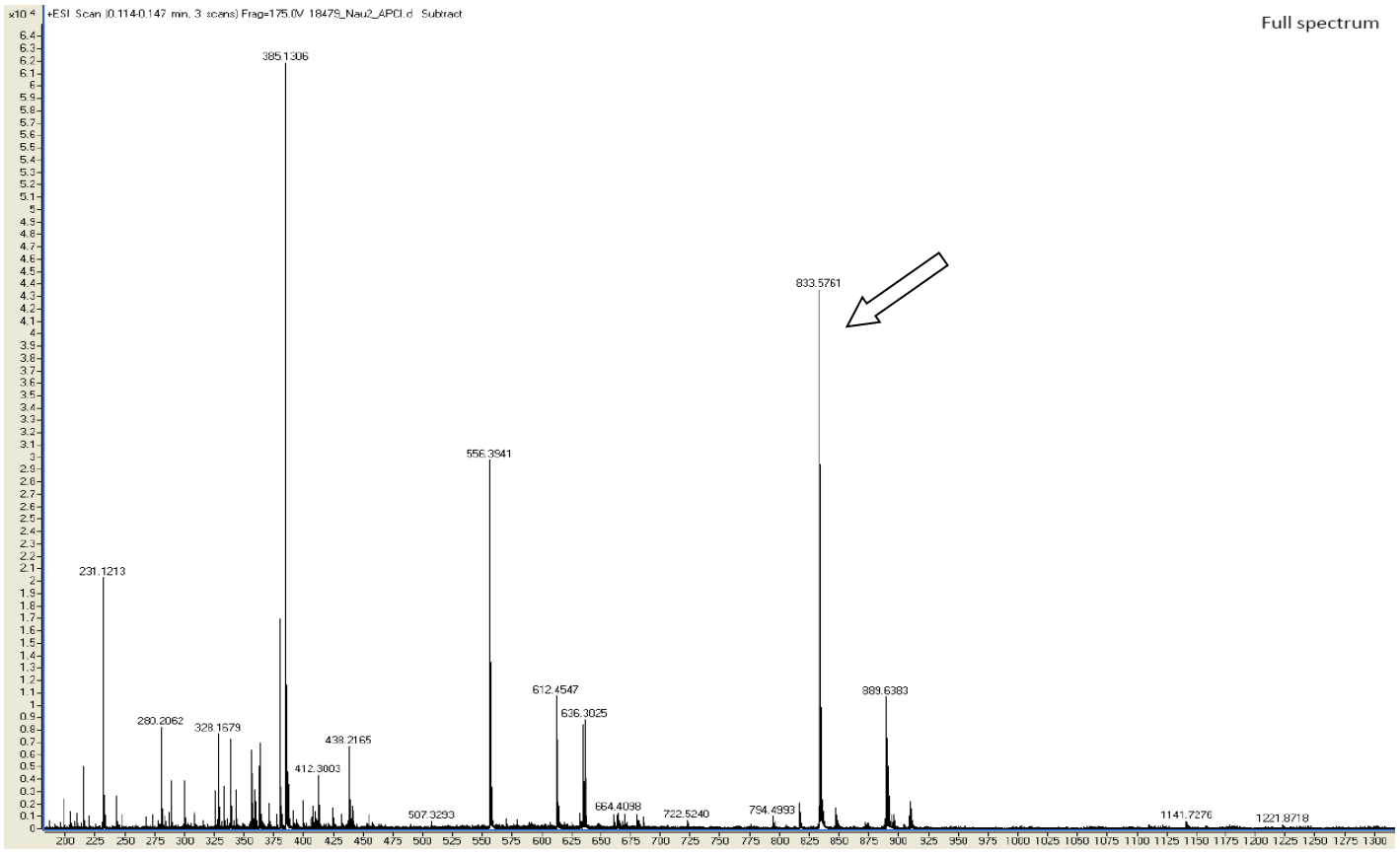

Fig. S6APCI-MS of **CCF**

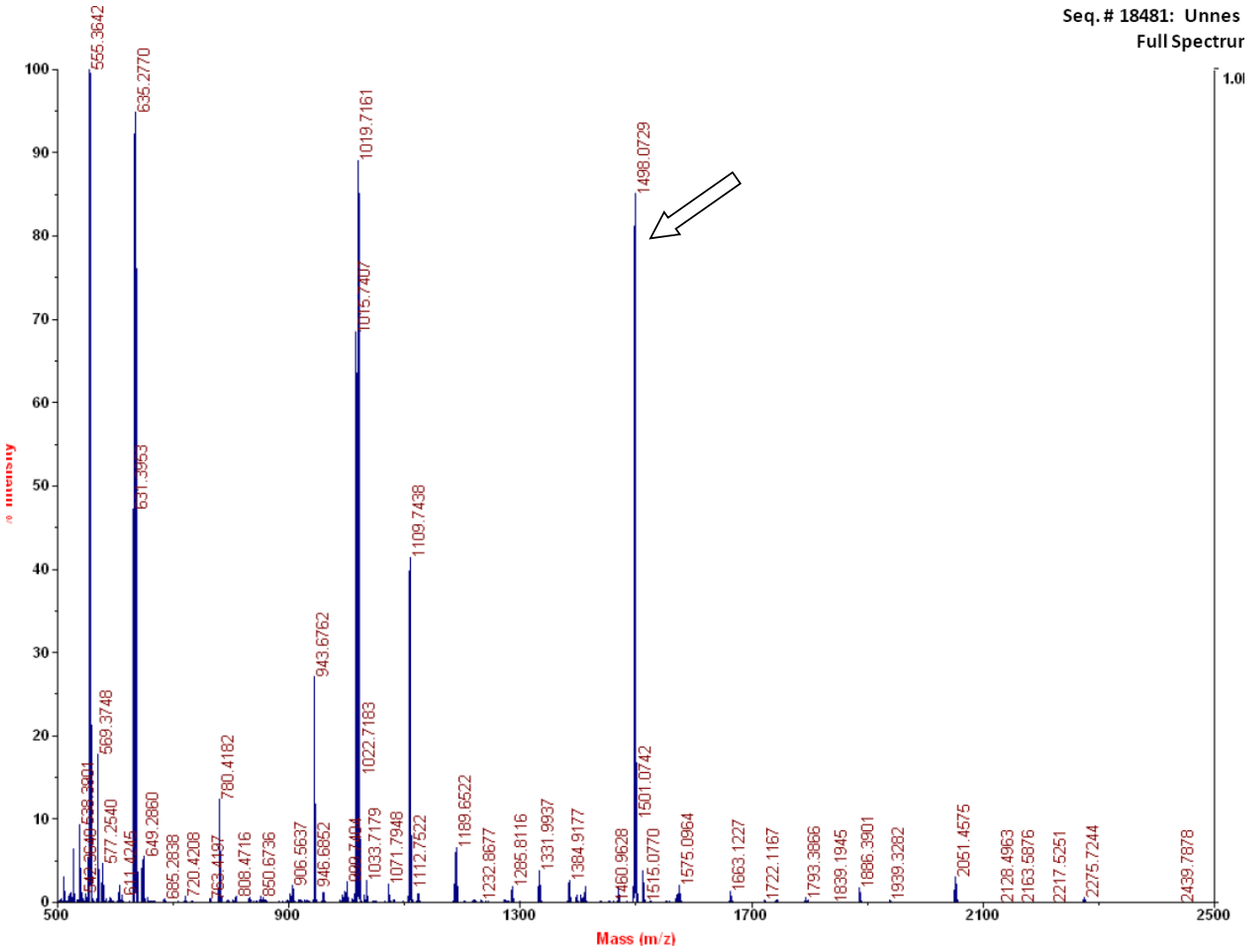

Fig. S7MALDI-TOF of **CFD**

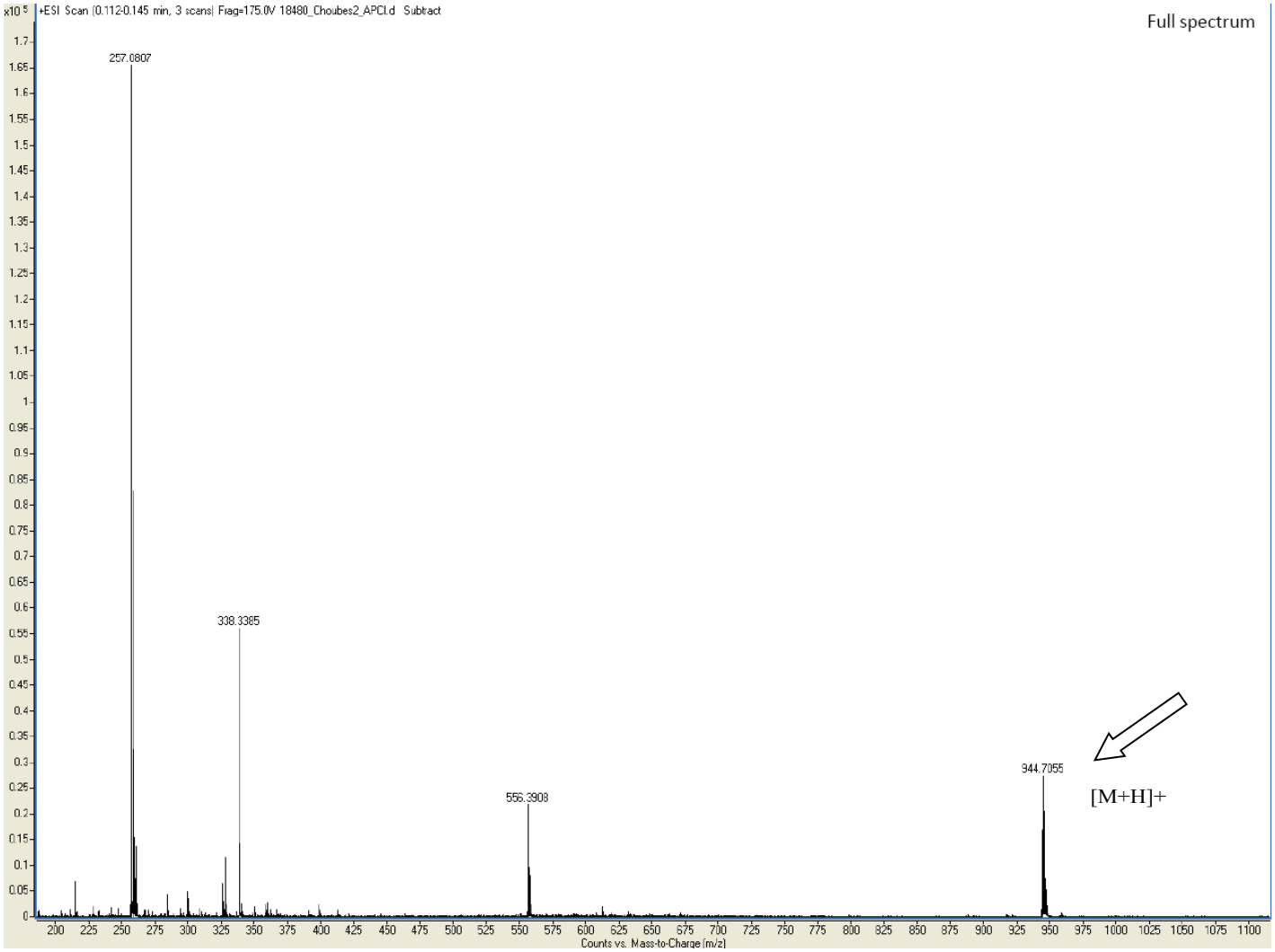

Fig. S8APCI-MS of **CFM**