

Supplementary Files

Simple Route to Synthesize Fully Conjugated Ladder Isomer Copolymers with Carbazole Units

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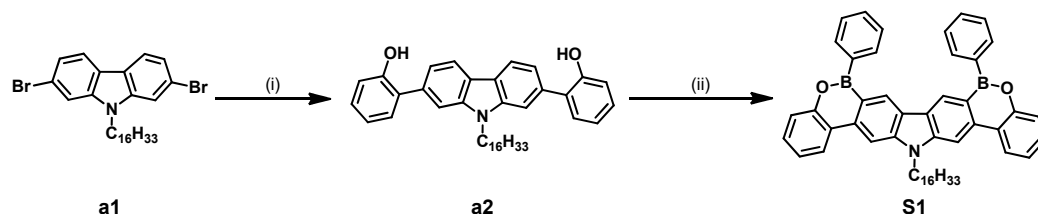
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Materials and Instruments

Commercial chemicals were used without further purification. Tetrahydrofuran (THF), and dichloromethane (DCM) were distilled by a standard process before using. The reactions were monitored by thin layer chromatography (TLC) with silica gel 60 F254 (Merck, 0.2 mm). ¹H and ¹³C NMR data were acquired on a Bruker AV600 spectrometer. The electrochemical behavior was recorded by cyclic voltammetry (Holland, Ivium Plus II) with a standard three-electrode electrochemical cell. A glassy carbon working electrode, a Pt wire counter electrode, and an Ag/Ag⁺ (0.01 M in CH₃CN) reference electrode. UV-visible absorption spectra were obtained on a Shimadzu UV-visible spectrometer model UV-2550. Fluorescence spectra were investigated by a Shimadzu RF-5301PC fluorescence spectrophotometer. MALDI-TOF analyses were obtained by Bruker Daltonics Inc Autoflex III. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were carried out under nitrogen on Perkin-Elmer Pyris 6 TGA (heating rate of 10 °C/min) and Perkin-Elmer Diamond DSC instruments (scanning rate of 10 °C/min), respectively, to record TGA and DSC curves.

Experimental Section



Scheme S1. The synthetic routes to compound S1. (i) NaHCO₃, THF/H₂O, Pd(PPh₃)₄, reflux, 12h. (ii) TEA, *o*-DCB, reflux, 12h.

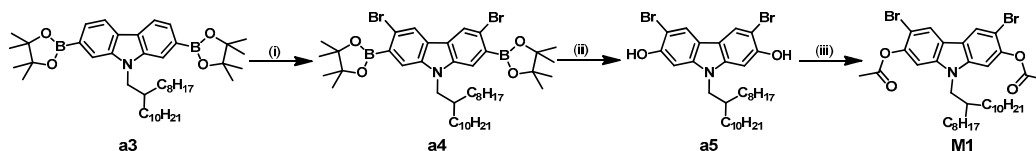
Compound a2

A mixture of compound **a1** (0.30 g, 0.55 mmol), 2-hydroxyphenylboronic acid (0.60 g, 0.93 mmol), NaHCO₃ (0.35 g), THF (25 mL) and H₂O (4 mL) was degassed, Pd(PPh₃)₄ (12 mg, 0.01 mmol) was added under a nitrogen atmosphere. The mixture was heated at reflux and stirred under nitrogen for 12 h. After cooling, water and CH₂Cl₂ (200 mL) were added, the organic layer was separated and dried over Na₂SO₄. After removal of the solvent, the residue was chromatographically purified on silica gel eluting with petroleum ether/dichloromethane (v/v=1/3) to afford compound **a3** (0.26 g, 83 %). ¹H NMR (600 MHz, CDCl₃, ppm): δ = 8.15 (d, J = 7.9 Hz, 2H), 7.42 (s, 2H), 7.31 (dd, J = 7.9, 1.5 Hz, 2H), 7.28 (dd, J = 7.9, 1.2 Hz, 2H), 7.25 (td, J = 7.9,

1.5 Hz, 2H), 6.98 (t, $J = 7.1$ Hz, 4H), 5.41 (s, 2H), 4.25 (t, $J = 7.3$ Hz, 2H), 1.84 – 1.78 (m, 2H), 1.33 – 1.28 (m, 2H), 1.25 – 1.20 (m, 4H), 1.15 (d, $J = 17.8$ Hz, 21H), 0.80 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (150MHz, CDCl_3 , ppm): $\delta = 151.60, 140.52, 133.70, 129.43, 128.16, 127.86, 121.18, 120.38, 119.79, 118.95, 114.77, 108.37, 42.29, 30.90, 28.77, 28.23, 27.98, 26.33, 21.66, 13.09$; MS (MALDI-FTICR): m/z : calcd for $\text{C}_{40}\text{H}_{49}\text{NO}_2$: 575.8200 $[\text{M}]^+$; found: 576.3757.

Compound S1

A mixture of compound a2 (0.20g, 0.35mmol), phenylboron dichloride (0.17g, 1.05mmol), Triethylamine (8 drops) and 1,2-dichlorobenzene (10 mL) were heated at reflux and stirred under nitrogen for 6 h. After removal of the solvent, the residue was chromatographically purified on silica gel eluting with petroleum ether/dichloromethane ($v/v=1/1$) to afford compound S1 (0.25 g, 96%). ^1H NMR (600 MHz, CDCl_3 , ppm): $\delta = 9.03$ (s, 2H), 8.33 (d, $J = 7.8$ Hz, 2H), 8.14 (d, $J = 5.6$ Hz, 4H), 8.11 (s, 2H), 7.60 (d, $J = 5.9$ Hz, 6H), 7.55 (d, $J = 8.0$ Hz, 2H), 7.46 (t, $J = 7.4$ Hz, 2H), 7.34 (t, $J = 7.4$ Hz, 2H), 4.40 (t, $J = 6.9$ Hz, 2H), 2.02~1.95 (m, 2H), 1.50~1.45 (m, 2H), 1.42~1.38 (m, 2H), 1.26 (d, $J = 7.0$ Hz, 8H), 1.22 (d, $J = 11.0$ Hz, 14H), 0.87 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3 , ppm): $\delta = 151.51, 145.06, 138.03, 134.53, 130.32, 130.05, 128.91, 128.16, 123.65, 123.41, 123.18, 123.08, 120.66, 100.74, 43.08, 31.93, 29.66, 29.54, 29.40, 29.36, 28.66, 27.30, 22.70, 14.12$; MS (MALDI-FTICR): m/z : calcd for $\text{C}_{52}\text{H}_{55}\text{B}_2\text{NO}_2$: 747.6200; found: 747.4420.



Scheme S2. The synthetic routes to compound M1. (i) NBS, DMF, 110 °, 30 min. (ii) acetone, H_2O_2 , NaOH. (iii) DCC, DMAP, THF/ CH_3COOH , 45 °C, 12h.

Compound a4

A mixture of compound a3 (0.70 g, 1.00 mmol), NBS (0.39 g, 2.20 mmol) and 25 mL DMF was heated at 110 °C and stirred under nitrogen for 30 min. After cooling, water and CH_2Cl_2 (200 mL) were added, the organic layer was separated and dried over Na_2SO_4 . After removal of the solvent, the residue was chromatographically purified on silica gel eluting with petroleum ether/dichloromethane ($v/v=1/1$) to afford compound a4 (0.68 g, 80 %). ^1H NMR (600 MHz, CDCl_3 , ppm): $\delta = 8.18$ (s, 2H), 7.66 (s, 2H), 4.16 (d, $J = 7.1$ Hz, 2H), 2.06 (s, 1H), 1.32 (d, $J = 62.5$ Hz, 56H), 0.87 (q, $J = 5.1, 4.6$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): $\delta = 139.76, 124.77, 124.67, 117.21, 116.90, 84.30, 37.95, 31.92, 31.88, 31.85, 29.89, 29.62, 29.53, 29.34, 29.27, 26.52, 24.84, 22.68, 22.66, 14.11$; MS (MALDI-TOF): m/z : calcd for $\text{C}_{44}\text{H}_{69}\text{B}_2\text{Br}_2\text{NO}_4$: 857.5 $[\text{M}]^+$; found: 856.9.

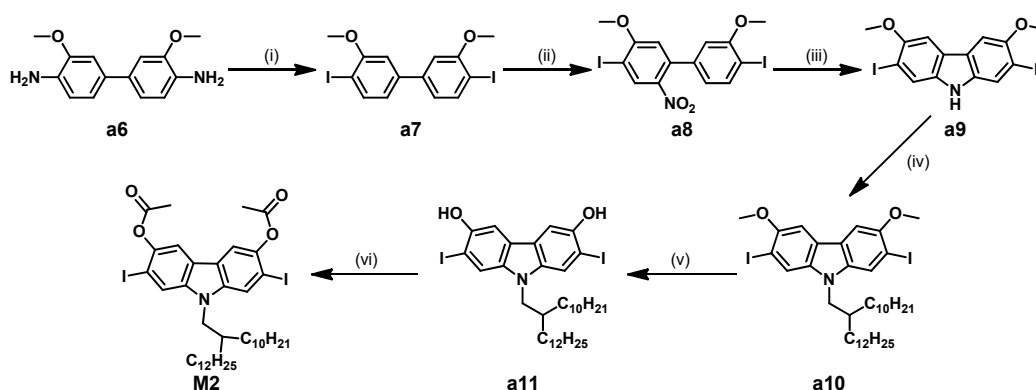
Compound a5

Compound a4 (0.50 g, 0.58 mmol) was dissolved in acetone (15 mL) and H_2O_2 (1.5 mL) was added in the mixture. Then NaOH aqueous solution (1.7 M, 1.5 mL) was added and stirred at room temperature for 15 min. After that, water and CH_2Cl_2 (200 mL) were added, the organic layer was separated and dried over Na_2SO_4 . After removal of the solvent, the residue was chromatographically purified on silica gel eluting with petroleum ether/dichloromethane ($v/v=1/1$)

to afford compound a5 (0.32 g, 86 %). ^1H NMR (600 MHz, CDCl_3 , ppm): δ = 7.94 (s, 2H), 6.94 (s, 2H), 5.63 (s, 2H), 3.92 (d, J = 7.5 Hz, 2H), 2.03 (s, 1H), 1.22 (d, J = 18.0 Hz, 32H), 0.87 (dt, J = 6.8, 3.0 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 150.16, 142.15, 122.27, 117.22, 102.10, 95.99, 95.97, 48.23, 37.43, 31.92, 31.85, 31.82, 29.91, 29.59, 29.58, 29.50, 29.45, 29.32, 29.23, 26.54, 22.69, 22.65, 14.12; MS (MALDI-TOF): m/z : calcd for $\text{C}_{32}\text{H}_{47}\text{Br}_2\text{NO}_2$: 637.5 $[\text{M}]^+$; found: 636.8.

Compound M1

Compound a5 was dissolved in THF (25 mL) with 0.1 mL of CH_3COOH . DCC (0.26 g, 1.26 mmol) and DMAP (0.06 g, 0.50 mmol) were added in batches. Then the mixture was heated at 45 $^\circ\text{C}$ for 12 hours. After cooling, removal of the solvent, the residue was chromatographically purified on silica gel eluting with petroleum ether/dichloromethane ($v/v=1/3$) to afford compound M1 (0.26 g, 83 %). ^1H NMR (600 MHz, CDCl_3 , ppm): δ = 8.14 (s, 2H), 7.09 (s, 2H), 3.95 (s, 2H), 2.42 (s, 6H), 1.99 (s, 1H), 1.20 (s, 32H), 0.88 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 168.88, 146.32, 140.93, 124.30, 120.81, 106.81, 104.46, 104.43, 37.65, 31.92, 31.87, 31.73, 29.86, 29.62, 29.57, 29.54, 29.48, 29.33, 29.22, 26.42, 22.70, 22.65, 20.96, 20.92, 14.12; MS(MALDI- FTICR): m/z : calcd for $\text{C}_{36}\text{H}_{51}\text{Br}_2\text{NO}_4$: 721.6000 $[\text{M}]^+$; found: 721.2158.



Scheme S3. The synthetic routes to compound M2. (i) HCl, NaNO_2 , rt, 30 min, KI, rt, 12h. (ii) HNO_3 , CH_2Cl_2 , 70 $^\circ\text{C}$. (iii) triethyl phosphite, *o*-DCB (6 mL), reflux, 12h. (iv) NaH, DMF, 30 $^\circ\text{C}$, 4 h. (v) BBr_3 , CH_2Cl_2 , 30 $^\circ\text{C}$, 2 h. (vi) DCC, DMAP, THF/ CH_3COOH , 45 $^\circ\text{C}$, 12h.

Compound a7

Compound a6 was dissolved in HCl aqueous solution and NaNO_2 (6.20 g, 89.86 mmol) was slowly added into the mixture. If some suspended matter were occurred in the solution, more HCl aqueous solution was needed to make the solution clarification. Then the mixture was stirred at room temperature for 30 min. KI (17.00 g, 0.10 mol) was added and stirred at room temperature for 12 hours. After cooling, water and CH_2Cl_2 (200 mL) were added, the organic layer was separated and dried over Na_2SO_4 . After removal of the solvent, the residue was chromatographically purified on silica gel eluting with petroleum ether to afford compound a7 (2.50 g, 26 %). ^1H NMR (600 MHz, CDCl_3 , ppm): δ = 7.82 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 1.5 Hz, 2H), 6.90 (dd, J = 8.0, 1.7 Hz, 2H), 3.95 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3 , ppm): δ = 158.55, 142.42, 139.78, 121.30, 109.83, 85.43, 56.47.

Compound a8

Compound (2.50 g, 5.36 mmol) was dissolved in CH_2Cl_2 (20 mL). Dilute HNO_3 solution was

added and the reaction was heated at 70 °C. The reaction was detected by TCL until the reaction finished. After cooling, water and CH₂Cl₂ (200 mL) were added, the organic layer was separated and dried over Na₂SO₄. After removal of the solvent, the residue was chromatographically purified on silica gel eluting with petroleum ether/dichloromethane (v/v=3/1) to afford compound a8 (2.20 g, 81 %). ¹H NMR (600 MHz, CDCl₃, ppm): δ = 8.44 (s, 1H), 7.81 (d, J = 7.9 Hz, 1H), 6.69 (d, J = 2.7 Hz, 2H), 6.65 (dd, J = 7.9, 1.7 Hz, 1H), 3.92 (d, J = 56.4 Hz, 6H); ¹³C NMR (150 MHz, CDCl₃, ppm): δ = 161.20, 158.23, 142.06, 139.70, 139.32, 138.47, 135.96, 121.73, 112.59, 110.43, 86.36, 84.16, 57.16, 56.49.

Compound a9

A mixture of compound a8 (0.50 g, 0.98 mmol), triethyl phosphite (1.6 mL) and *o*-DCB (6 mL) was degassed. The mixture was heated at reflux and stirred under nitrogen overnight. After cooling, water and CH₂Cl₂ (200 mL) were added, the organic layer was separated and dried over Na₂SO₄. After removal of the solvent, the residue was chromatographically purified on silica gel eluting with petroleum ether/dichloromethane (v/v=10/9) to afford compound a9 (0.10 g, 21 %). ¹H NMR (600 MHz, CDCl₃, ppm): δ = 7.84 (s, 2H), 7.71 (s, 1H), 7.43 (s, 2H), 3.99 (s, 6H); ¹³C NMR (150 MHz, CDCl₃, ppm): δ = 152.09, 135.91, 123.77, 121.58, 101.61, 85.08, 57.12.

Compound a10

A mixture of compound a9 (0.10 g, 0.21 mmol), 11-(bromomethyl)tricosane (0.17 g, 0.42 mmol) and NaH (0.07 g) were dissolved in DMF (25 mL). The mixture was heated at 30 °C and stirred under nitrogen for 4 h. After cooling, water and CH₂Cl₂ (200 mL) were added, the organic layer was separated and dried over Na₂SO₄. After removal of the solvent, the residue was chromatographically purified on silica gel eluting with petroleum ether to afford compound a10 (0.16 g, 94 %). ¹H NMR (600 MHz, CDCl₃, ppm): δ = 7.75 (s, 2H), 7.45 (s, 2H), 3.99 (s, 8H), 2.05 (s, 1H), 1.24 (d, J = 11.5 Hz, 40H), 0.88 (t, J = 6.8 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 151.42, 137.18, 122.68, 119.96, 101.58, 84.92, 57.13, 47.83, 37.74, 31.96, 31.95, 31.60, 29.96, 29.71, 29.69, 29.66, 29.62, 29.40, 29.37, 26.36, 22.73, 14.17; MS (MALDI-FTICR): m/z: calcd for C₃₆H₅₁I₂NO₄: 815.6000 [M]⁺; found: 815.2624.

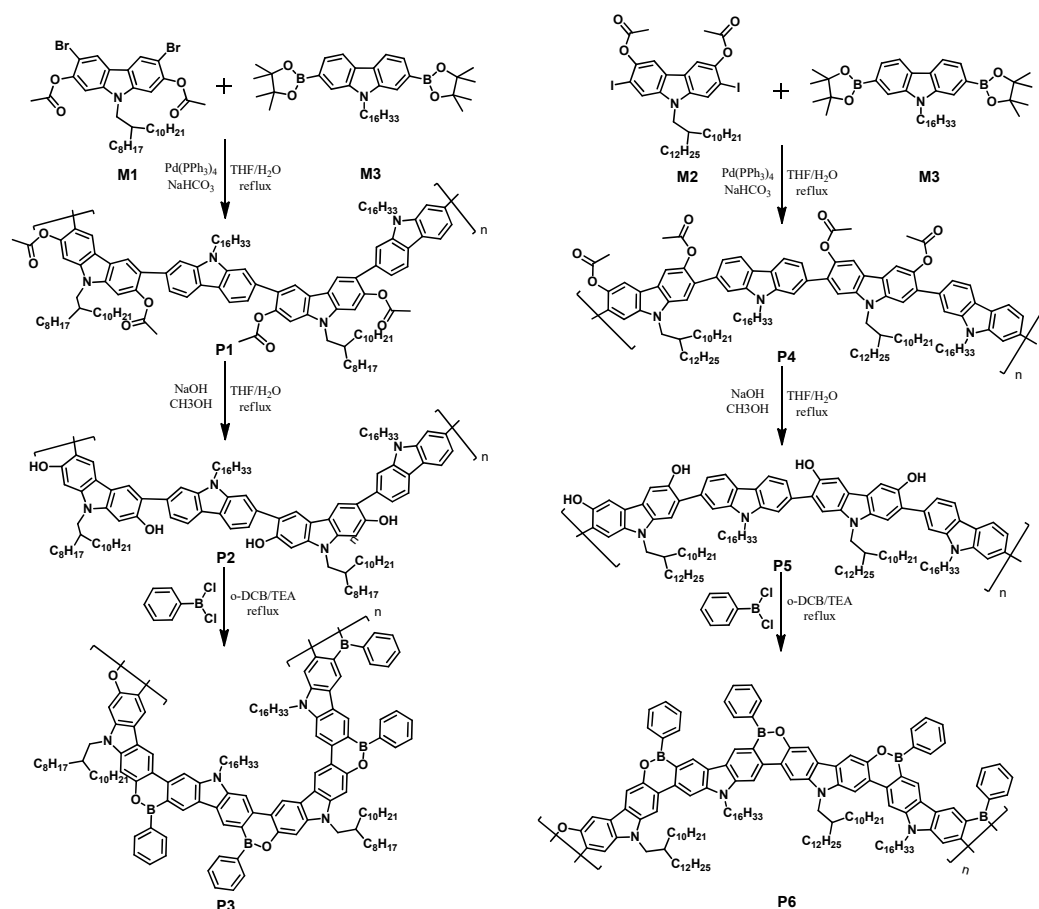
Compound a11

A mixture of compound a10 (0.14 g, 0.17 mmol) and BBr₃ (1.5 mL) were dissolved in CH₂Cl₂ (20 mL). The mixture was heated at 30 °C and stirred for 2 h. After cooling, water and CH₂Cl₂ (200 mL) were added, the organic layer was separated and dried over Na₂SO₄. After removal of the solvent, the residue was chromatographically purified on silica gel eluting with dichloromethane to afford compound a11 (0.10 g, 74 %). ¹H NMR (600 MHz, CDCl₃, ppm): δ = 7.59 (d, J = 2.0 Hz, 4H), 5.08 (s, 2H), 3.96 (d, J = 7.5 Hz, 2H), 2.02 (s, 1H), 1.24 (d, J = 10.5 Hz, 40H), 0.88 (t, J = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 147.54, 137.53, 123.69, 118.04, 84.80, 47.94, 37.59, 31.95, 31.93, 31.65, 29.94, 29.69, 29.67, 29.65, 29.60, 29.38, 29.35, 26.38, 22.71, 14.14; MS (MALDI-FTICR): m/z: calcd for C₃₆H₅₅I₂NO₂: 787.6400 [M]⁺; found: 786.2234.

Compound M2

Compound a11 (0.09 g, 0.11 mmol) was dissolved in THF (25 mL) with 0.1 mL of

CH₃COOH. DCC (0.14 g, 0.68 mmol) and DMAP (0.03 g, 0.27 mmol) were added in batches. Then the mixture was heated at 45 °C for 12 hours. After cooling, removal of the solvent, the residue was chromatographically purified on silica gel eluting with petroleum ether/dichloromethane (v/v=1/1) to afford compound M2 (0.09 g, 96 %). ¹H NMR (600 MHz, CDCl₃, ppm): δ = 7.77 (s, 2H), 7.71 (s, 2H), 4.03 (d, J = 7.4 Hz, 2H), 2.42 (s, 6H), 2.04 (s, 1H), 1.25 (s, 40H), 0.88 (t, J = 6.8 Hz, 6H); ¹³C NMR (75MHz, CDCl₃, ppm): δ = 169.59, 143.63, 140.21, 122.83, 119.46, 113.98, 88.26, 53.45, 48.06, 37.73, 31.95, 31.55, 29.96, 29.66, 29.40, 29.38, 26.37, 22.73, 21.37, 14.16; MS (MALDI-FTICR):m/z: calcd for C₄₀H₅₉I₂NO₄: 871.7100 [M]⁺; found: 870.2445.



Scheme S4. The synthetic routes to polymer P3 and P6

Polymer P1

A mixture of compound M1 (0.25 g, 0.35 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-hexadecyl-9H-carbazole M3 (0.23 g, 0.35 mmol), NaHCO₃ (0.35 g), THF (25 mL) and H₂O (4 mL) was degassed, Pd(PPh₃)₄ (12.80 mg, 0.01 mmol) was added under a nitrogen atmosphere. The mixture was heated by microwave reactor at reflux and stirred under nitrogen for 4 h. The solution was then cooled to room temperature, precipitated in methanol, and filtered. The solids were washed three times with methanol and

petroleum ether, respectively. Then dried to yield the polymer product P1 (0.31 g, 95%).

Polymer P2

A mixture of polymer P1 (0.25 g), NaOH (0.50 g), H₂O (2 mL), CH₃OH (3 mL) and THF (20 mL) were heated at reflux and stirred under nitrogen for 3 h. After cooling to the room temperature, the PH of solution was adjusted to 4~5. The solution was then cooled to room temperature, precipitated in methanol, and filtered. The solids were washed three times with methanol and petroleum ether, respectively. Then dried to yield the polymer product P2 (0.23 g, 96%).

Polymer P3

A mixture of polymer P2 (0.12 g), Phenylboron dichloride (0.1 mL), Triethylamine (5 drops) and 1,2-dichlorobenzene (10 mL) was heated at reflux and stirred under nitrogen for 3 h. The solution was then cooled to room temperature, precipitated in methanol, and filtered. The solids were washed three times with methanol and petroleum ether, respectively. Then dried to yield the final polymer product P3: brown solid (0.13 g, 92%)

Polymer P4

A mixture of compound M2 (0.075 g, 0.086 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-hexadecyl-9H-carbazole M3 (0.065 g, 0.086 mmol), NaHCO₃ (0.35 g), THF (25 mL) and H₂O (4 mL) was degassed, Pd(PPh₃)₄ (5 mg, 0.0043 mmol) was added under a nitrogen atmosphere. The mixture was heated by microwave reactor at reflux and stirred under nitrogen for 4 h. The solution was then cooled to room temperature, precipitated in methanol, and filtered. The solids were washed three times with methanol and petroleum ether, respectively. Then dried to yield the polymer product P4 (0.091 g, 93%).

Polymer P5

A mixture of polymer P4 (0.08 g), NaOH (0.50 g), H₂O (2 mL), CH₃OH (3 mL) and THF (20 mL) were heated at reflux and stirred under nitrogen for 3 h. After cooling to the room temperature, the PH of solution was adjusted to 4~5. The solution was then cooled to room temperature, precipitated in methanol, and filtered. The solids were washed three times with methanol and petroleum ether, respectively. Then dried to yield the polymer product P5 (0.07 g, 96%).

Polymer P6

A mixture of polymer P5 (0.05 g), Phenylboron dichloride (0.1 mL), Triethylamine (5 drops) and 1,2-dichlorobenzene (10 mL) was heated at reflux and stirred under nitrogen for 3 h. The solution was then cooled to room temperature, precipitated in methanol, and filtered. The solids were washed three times with methanol and petroleum ether, respectively. Then dried to yield the final polymer product P6: brown solid (0.06 g, 95%).

FTIR Spectra of Compounds

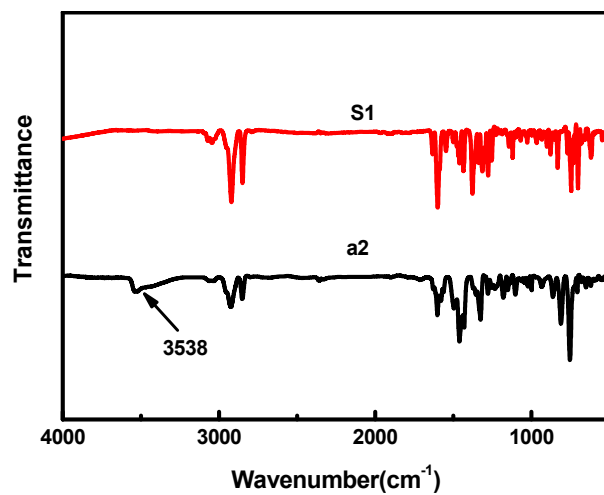


Figure S1. The FTIR spectra of compound a2 and S1

Photophysical Properties of Compounds

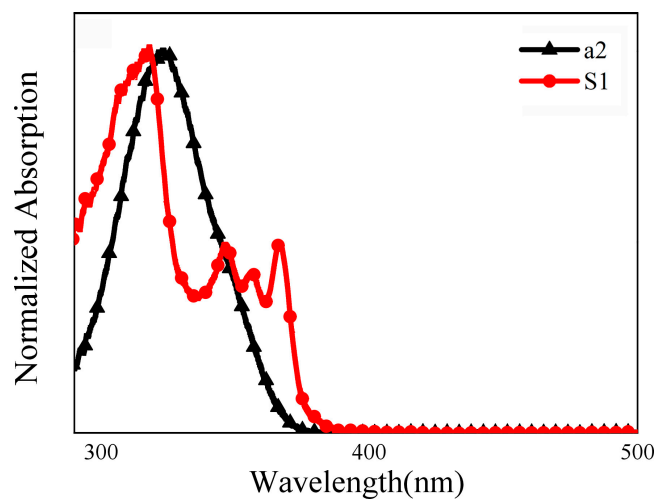


Figure S2. The UV-vis absorption spectra of compound a2 and S1

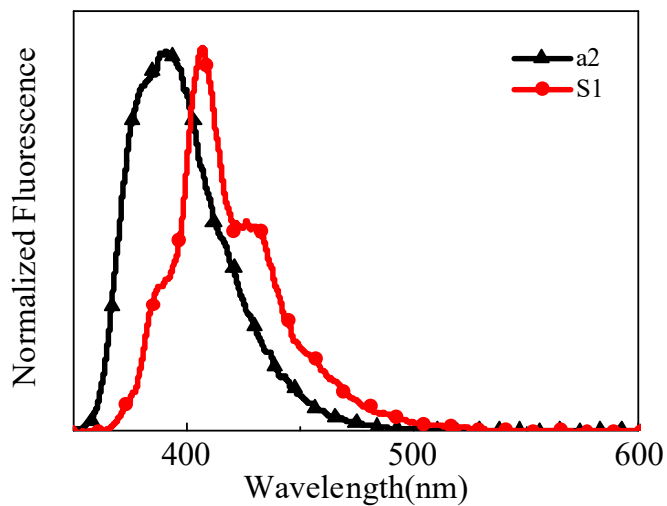


Figure S3. The fluorescence emission spectra of compound a2 and S1

Electrochemical Properties of Compounds and Polymers

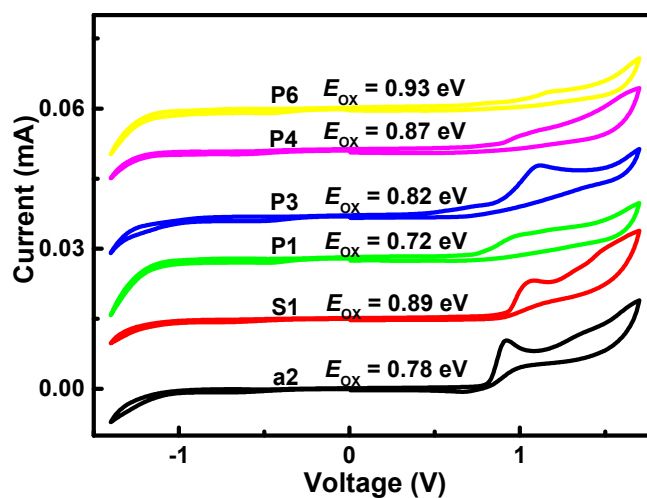


Figure S4. The cyclic voltammograms of compounds and polymers

Table S1. the CV date of compounds and polymers

	HOMO/eV	LUMO/eV	Band gap/eV
a2	-5.58	-2.19	3.39
S1	-5.69	-2.39	3.30
P1	-5.52	-2.38	3.14
P3	-5.62	-2.76	2.86
P4	-5.60	-2.60	3.00
P6	-5.68	-3.02	2.66

The NMR spectra and MALDI-TOF spectra

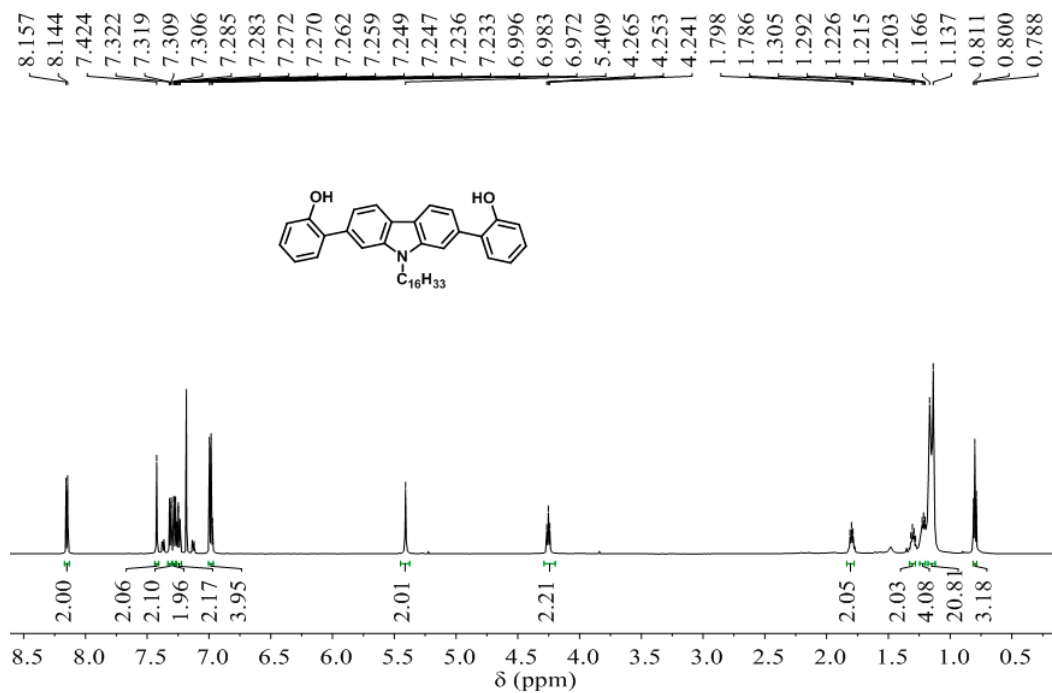


Figure S5. ¹H-NMR of the compound a2 recorded in CDCl₃.

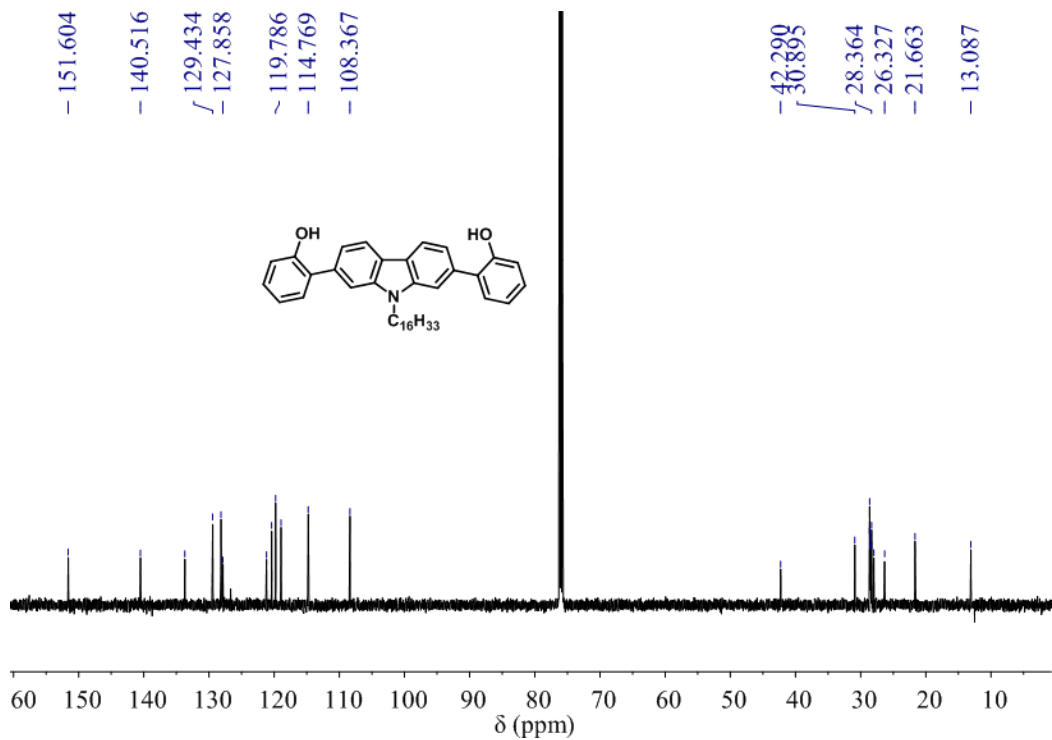


Figure S6. ¹³C-NMR of the compound a2 recorded in CDCl₃.

MALDI,LF3-188,20170313

Analysis Info

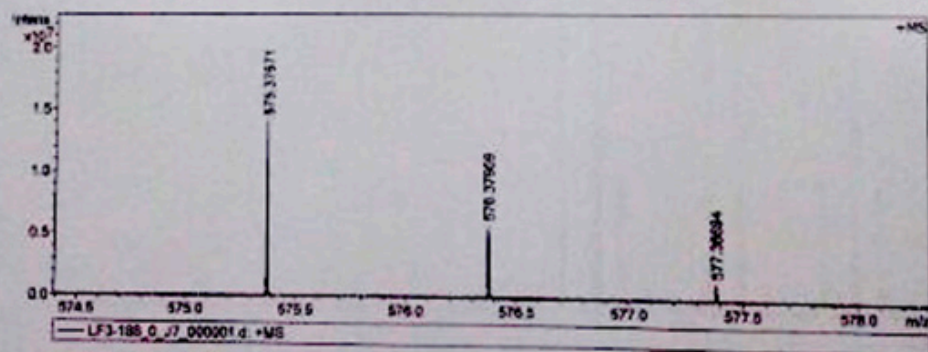
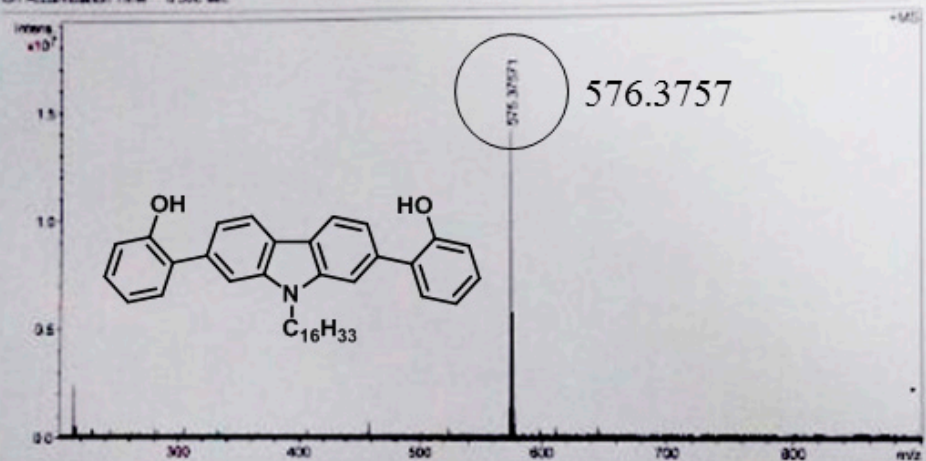
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 Sample Name:
 Comment:

Acquisition Date: 3/13/2017 6:39:56 PM

Operator:
 Instrument: solarix

Acquisition Parameter

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Broadband High Mass	900.0 m/z	Laser Power	32.2 %	Apodization	Gone-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				



Mass. m/z	#	Ion Formula	Score	m/z	err (ppm)	Mean err (ppm)	mSigma	ndb	a-Conf	N-Rule
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Figure S7. High resolution MALDI-TOF spectra of the a2.

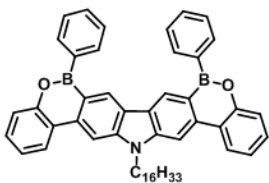
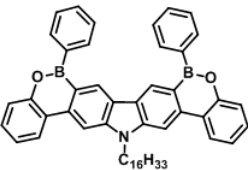
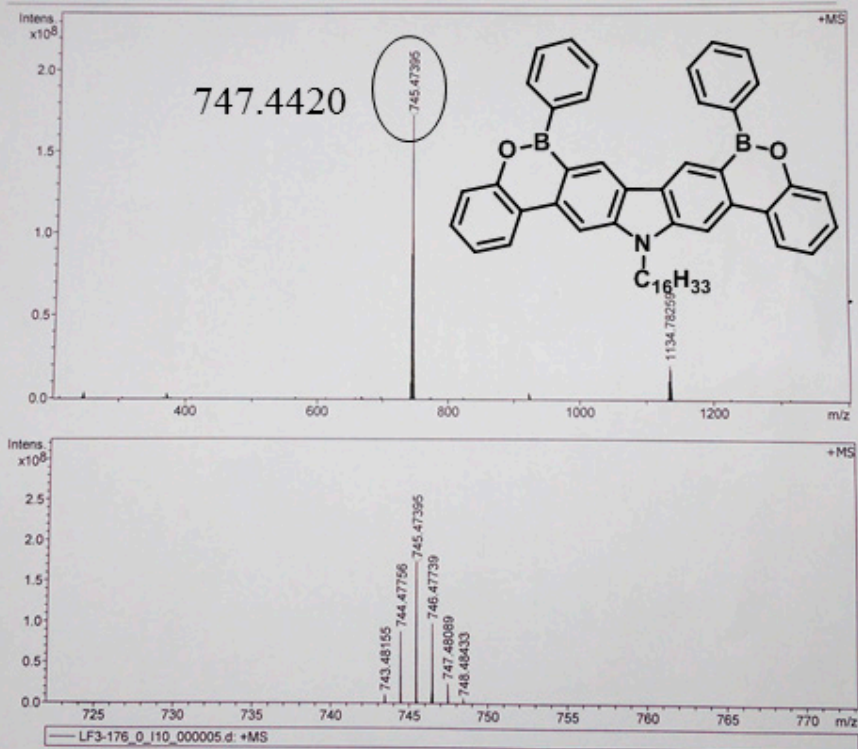


Figure S9. ^{13}C -NMR of the compound S1 recorded in CDCl_3 .

MALDI,LF3-176,20170110

Analysis Info
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 Instrument: solarix

Acquisition Parameter
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 Acquired Scans: 2
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 Laser Power: 25.2 lp
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 Calibration Date: Tue Jan 10 05:39:32
 Data Acquisition Size: 2097152
 Data Processing Size: 4194304
 Apodization: Sine-Bell Multiplication



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
745.473947	1	C ₅₂ H ₅₇ B ₂ N ₃	100.00	745.474951	-0.9	0.5	46.8	27.0	odd	ok

Figure S10. High resolution MALDI-TOF spectra of the S1.

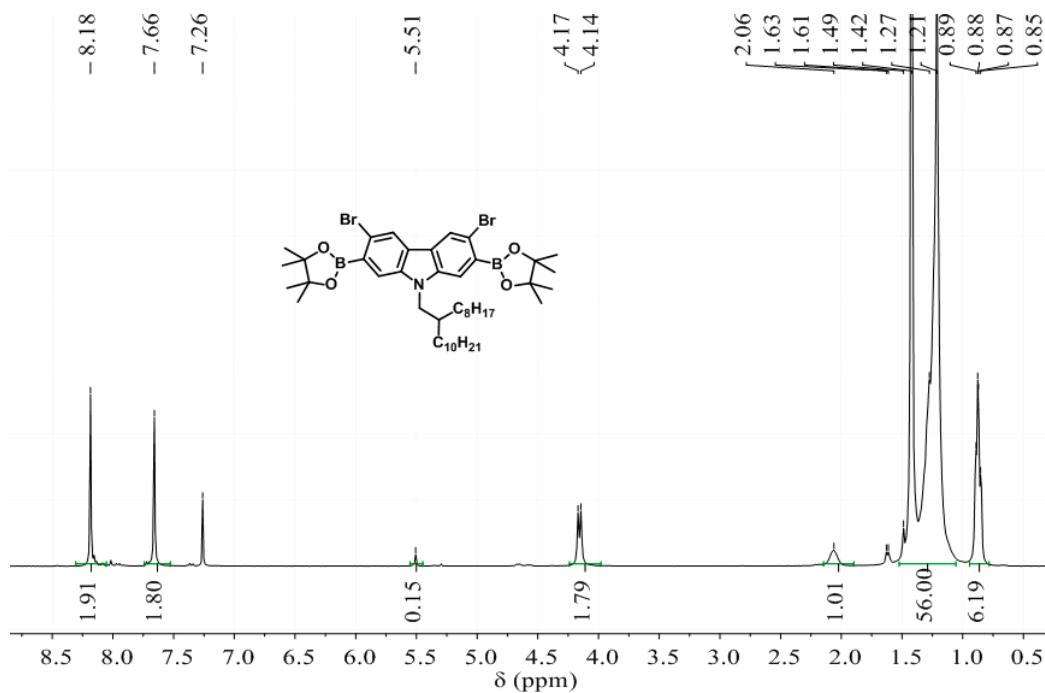


Figure S11. ¹H-NMR of the compound a4 recorded in CDCl₃.

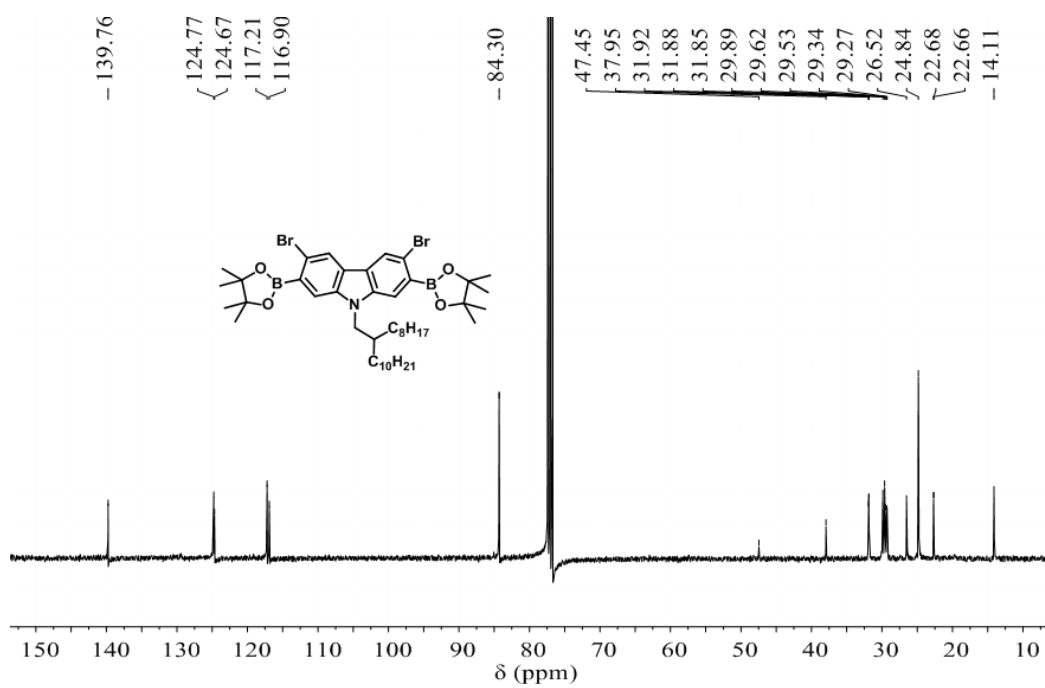


Figure S12. ¹³C-NMR of the compound a4 recorded in CDCl₃.

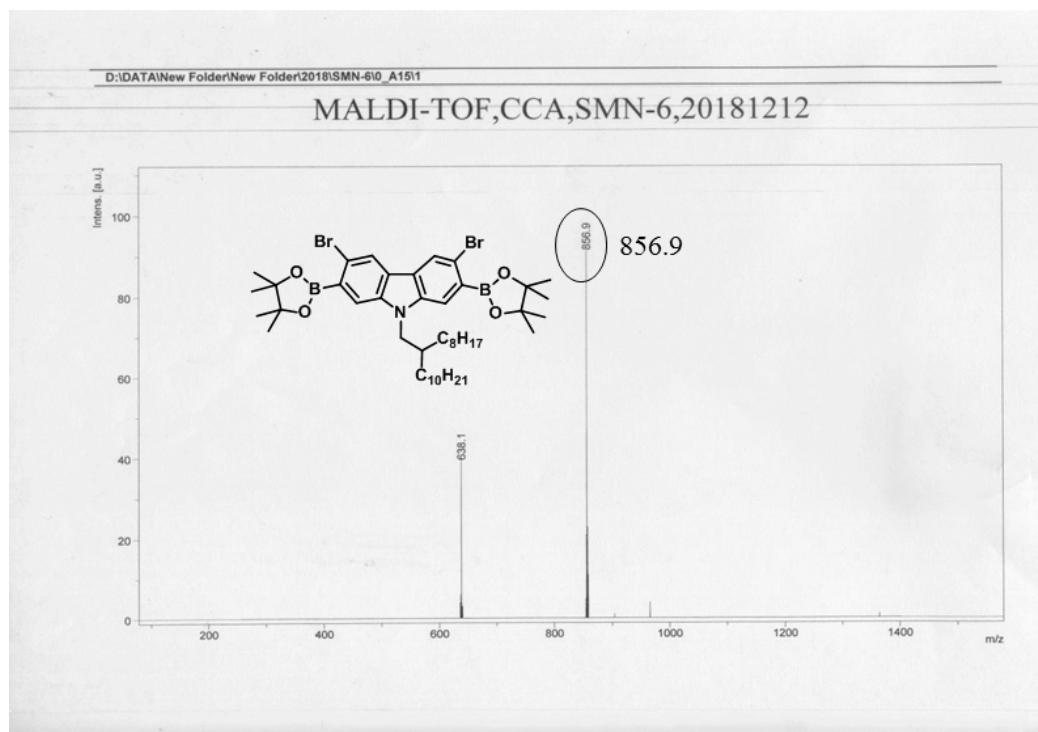


Figure S13. High resolution MALDI-TOF spectra of the a4.

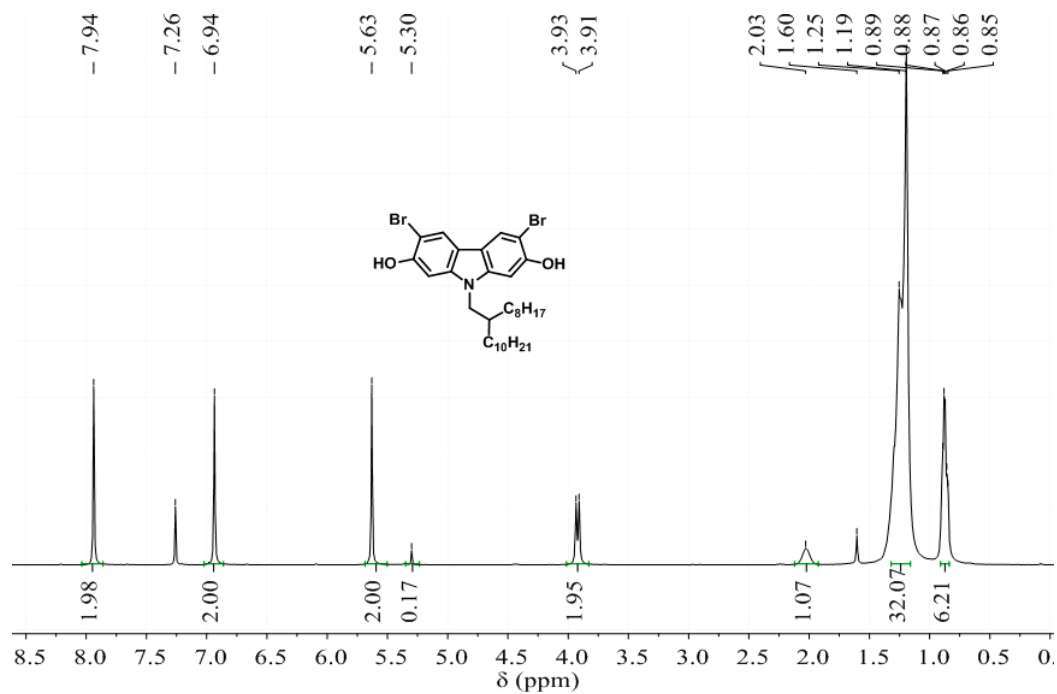


Figure S14. ^1H -NMR of the compound a5 recorded in CDCl_3 .

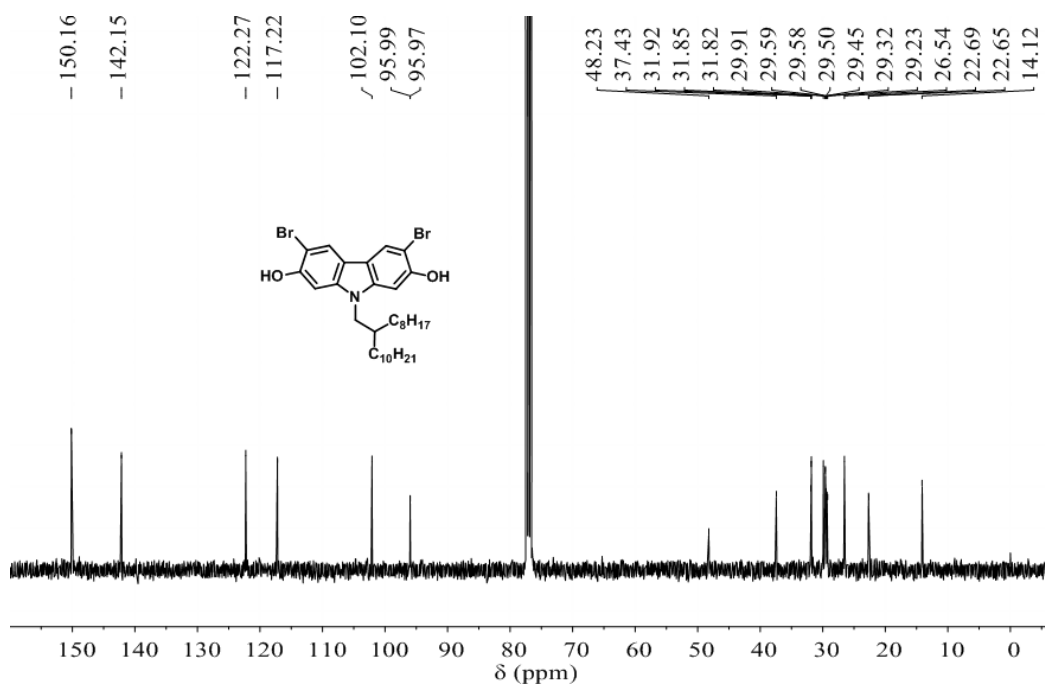


Figure S15. ^{13}C -NMR of the compound a5 recorded in CDCl_3 .

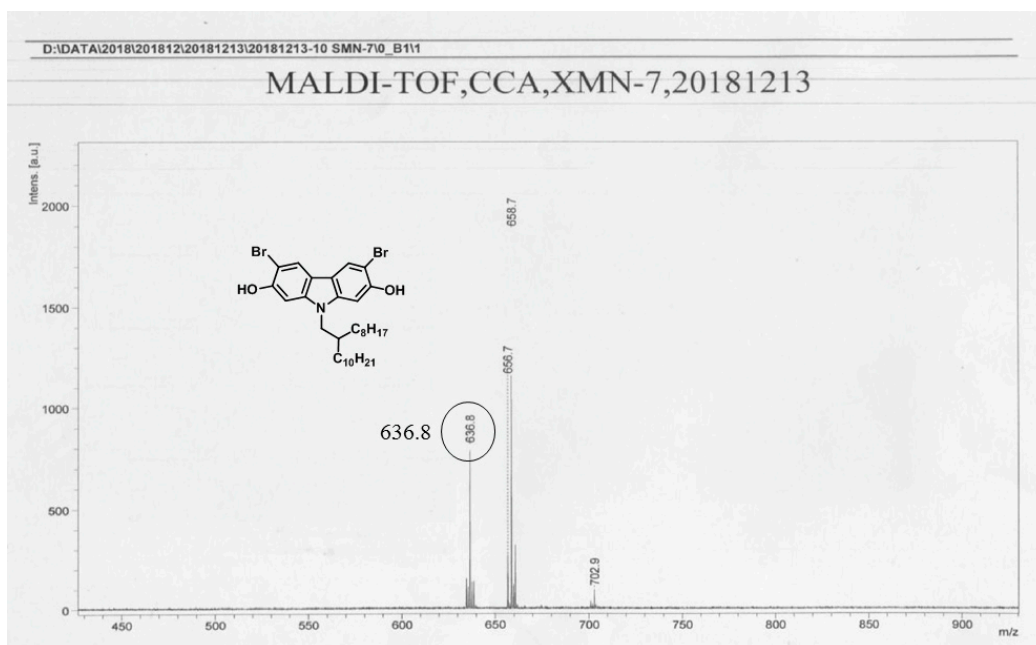


Figure S16. High resolution MALDI-TOF spectra of the a5.

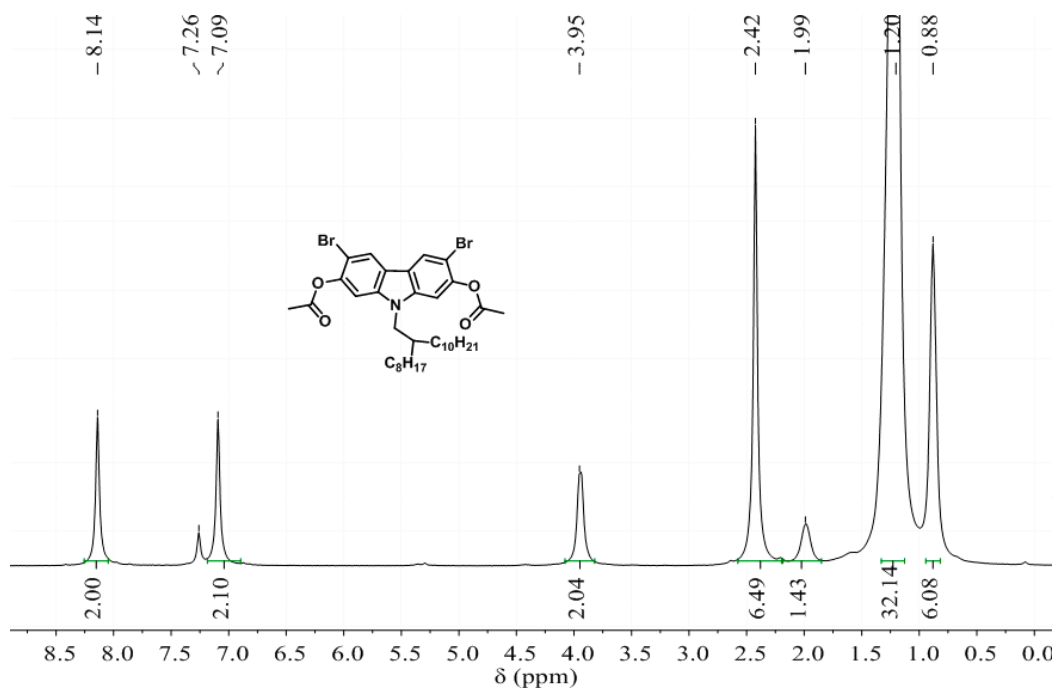


Figure S17. ¹H-NMR of the compound M1 recorded in CDCl₃.

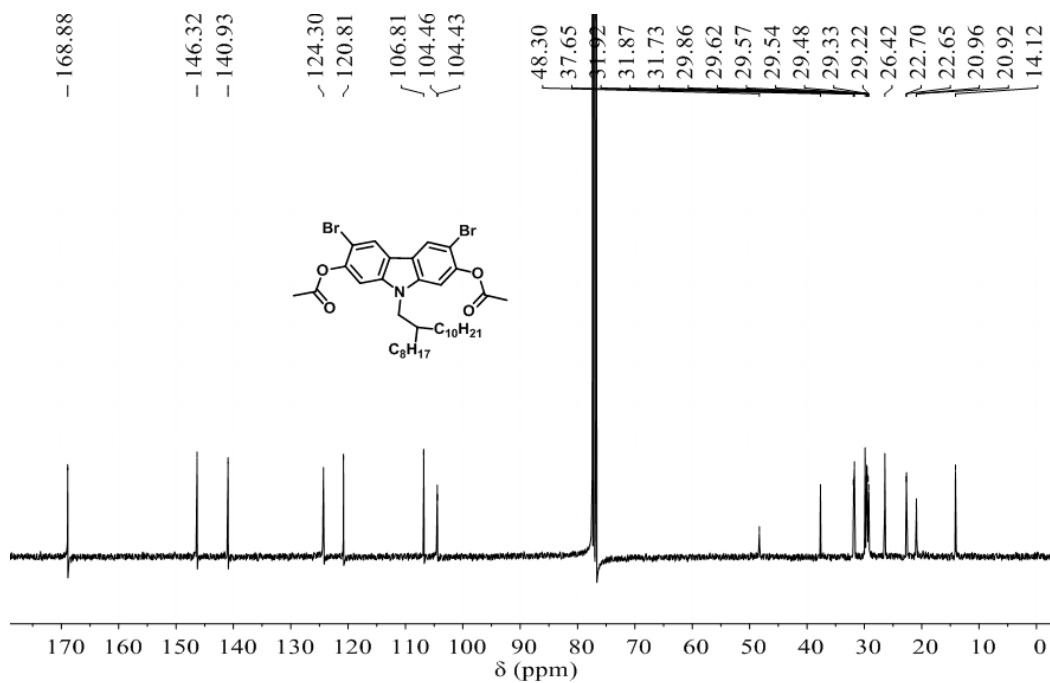


Figure S18. ¹³C-NMR of the compound M1 recorded in CDCl₃.

MALDI,MN-8,20181214

Analysis Info

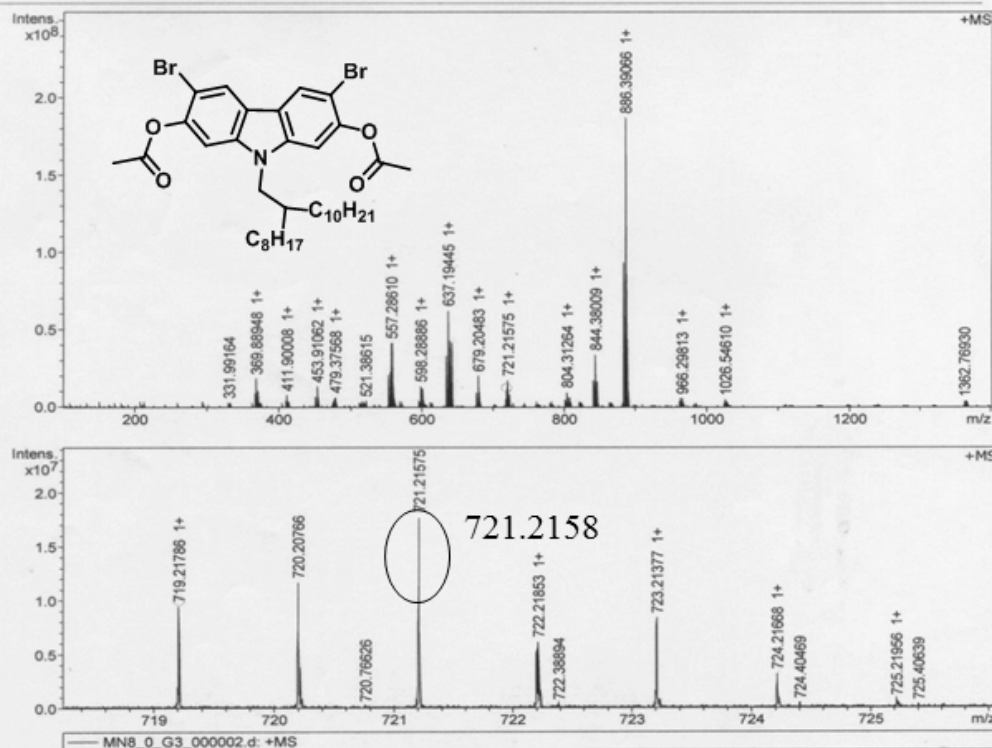
Analysis Name D:\Data\MALDI\2018\1214\MN8_0_G3_000002.d
Method MALDI_P_100-3000
Sample Name MURU-N-ESI
Comment

Acquisition Date 12/14/2018 5:20:06 PM

Operator
Instrument solarix

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	5	Calibration Date	Fri Dec 14 05:09:49 2018
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	101.1 m/z	No. of Laser Shots	15	Data Processing Size	4194304
Broadband High Mass	1400.0 m/z	Laser Power	44.8 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
719.217858	1	C36H51Br2NO4	100.00	719.217935	0.1		35.4	11.0	odd	ok

Figure S19. High resolution MALDI-TOF spectra of the M1.

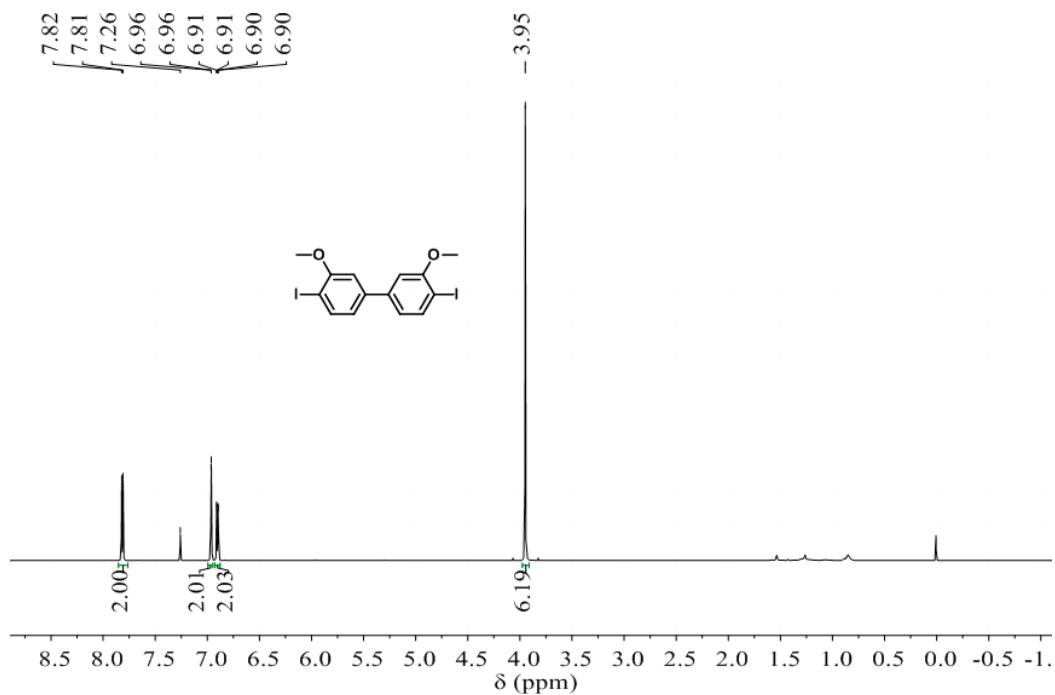


Figure S20. ^1H -NMR of the compound a7 recorded in CDCl_3 .

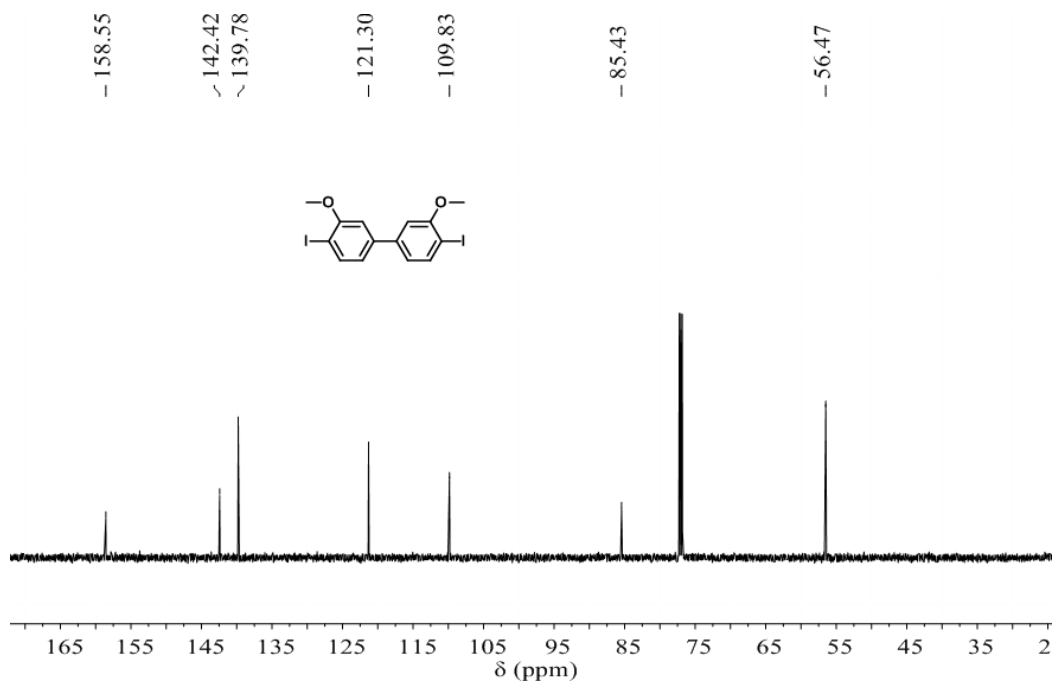


Figure S21. ^{13}C -NMR of the compound a7 recorded in CDCl_3 .

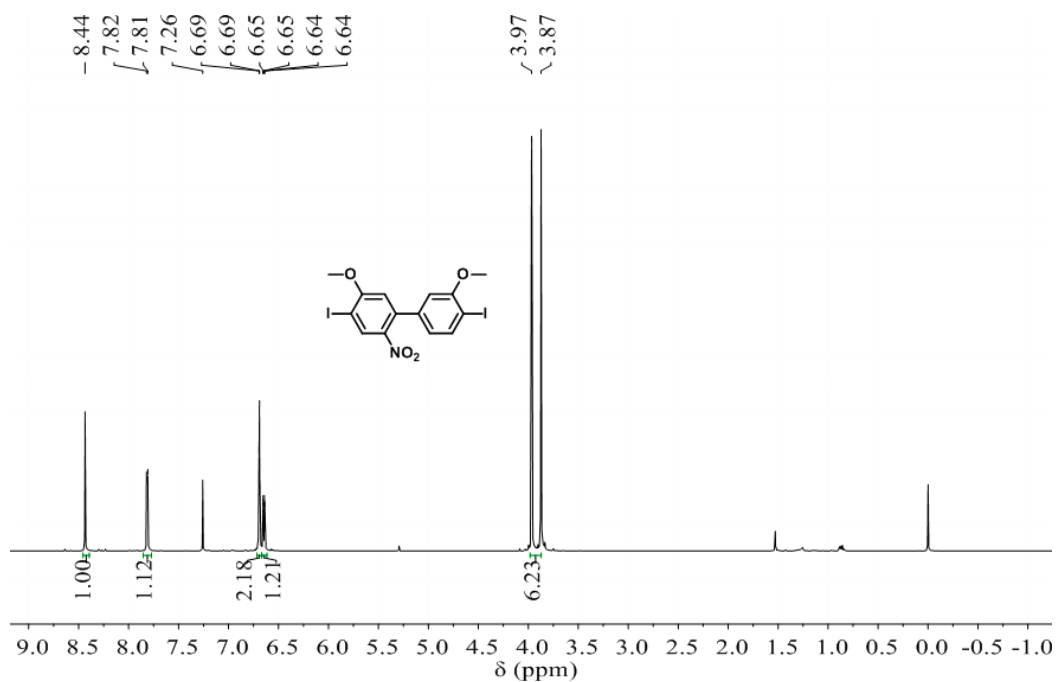


Figure S22. ¹H-NMR of the compound a8 recorded in CDCl₃.

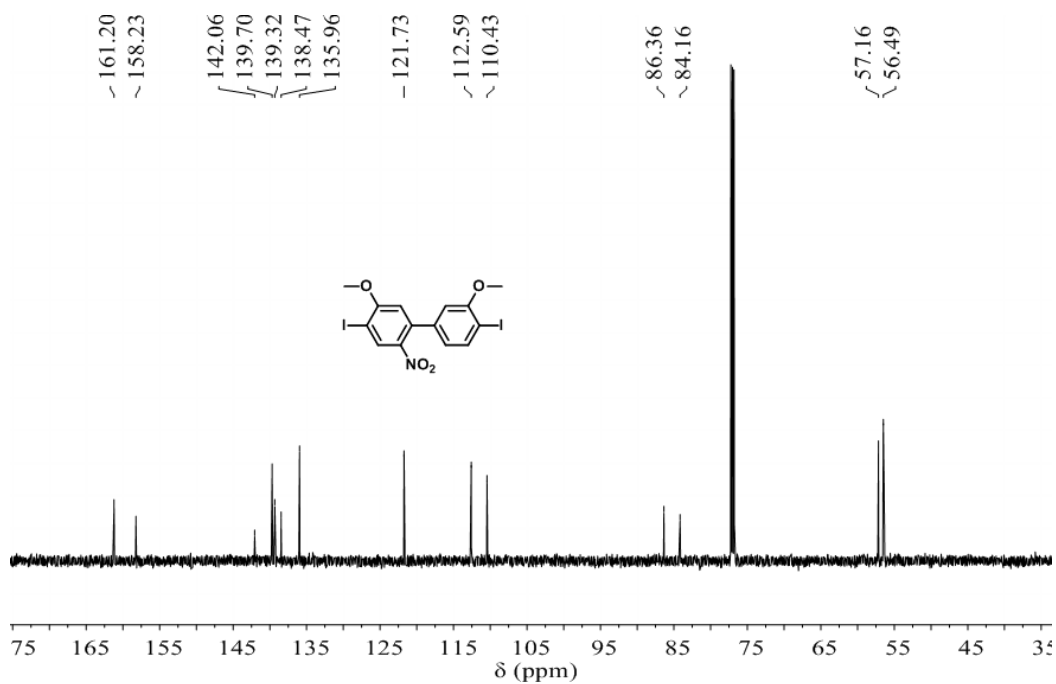


Figure S23. ¹³C-NMR of the compound a8 recorded in CDCl₃.

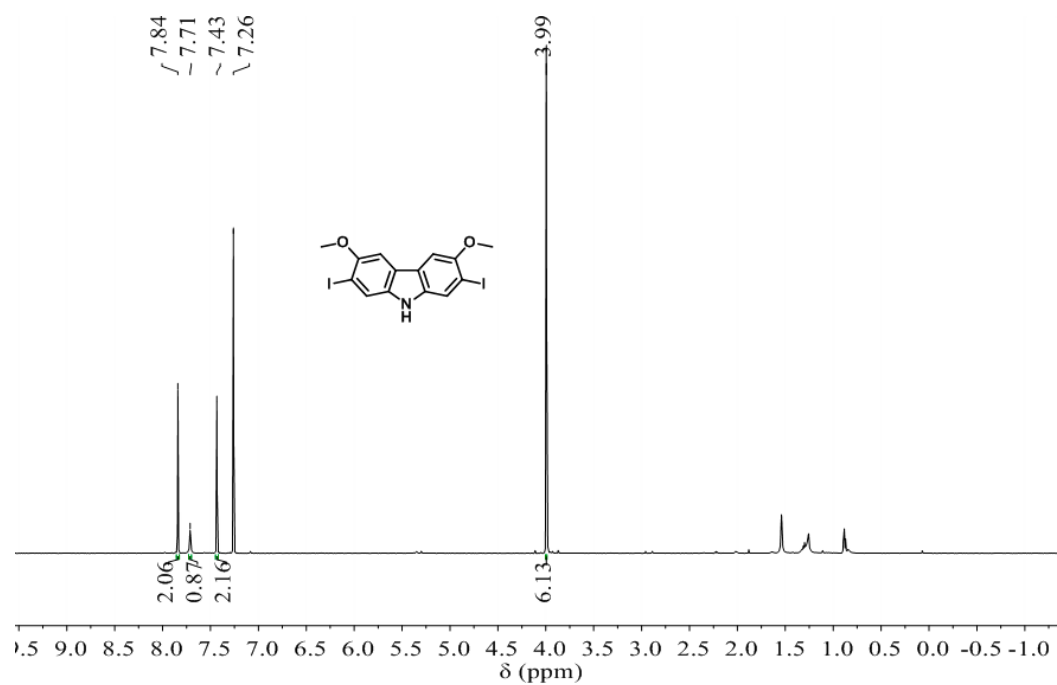


Figure S24. ¹H-NMR of the compound a9 recorded in CDCl₃.

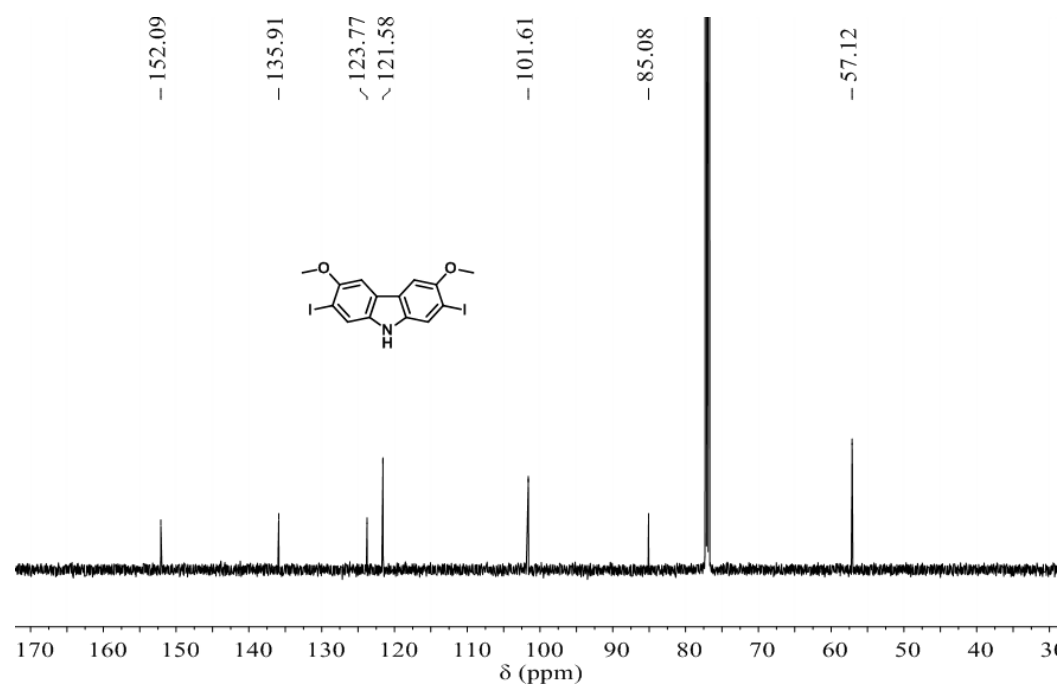


Figure S25. ¹³C-NMR of the compound a9 recorded in CDCl₃.

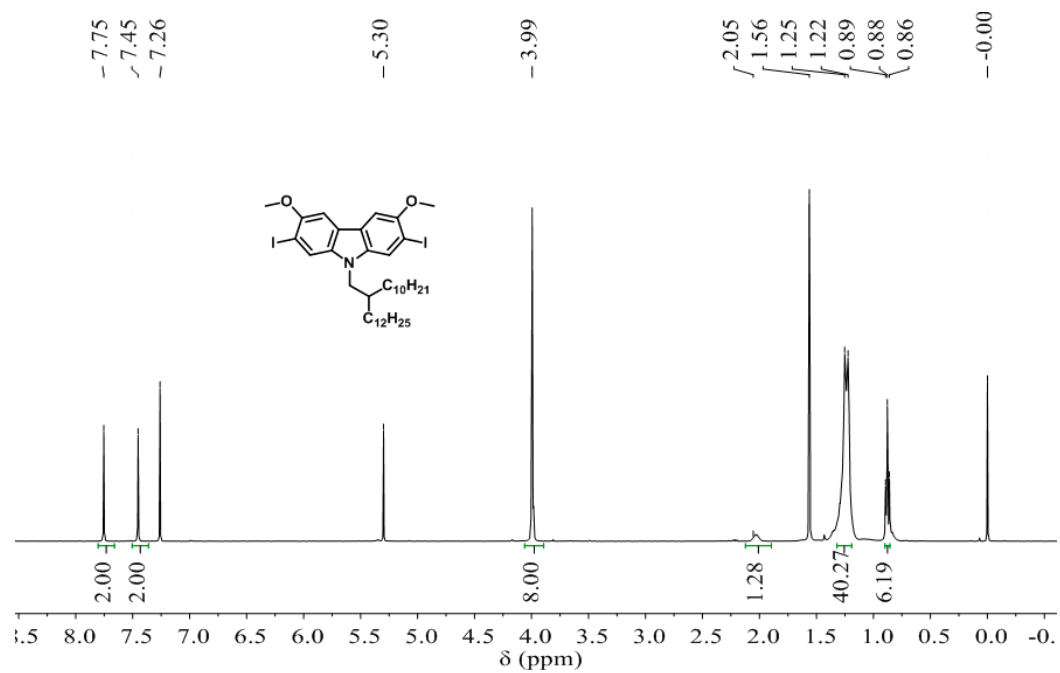


Figure S26. ¹H-NMR of the compound a10 recorded in CDCl₃.

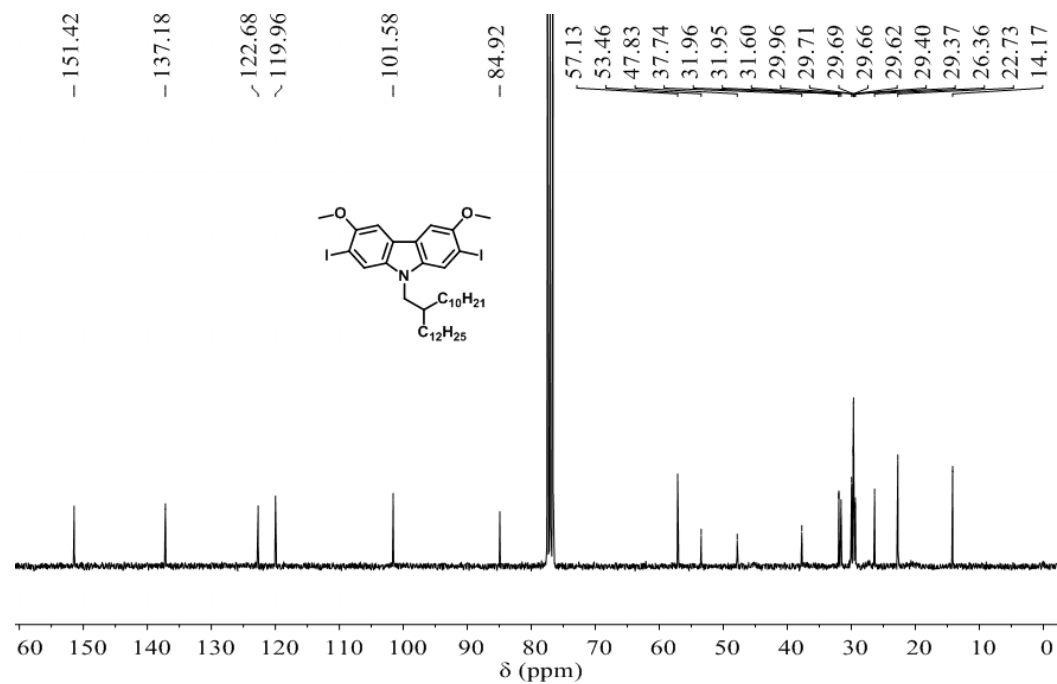


Figure S27. ¹³C-NMR of the compound a10 recorded in CDCl₃.

MALDI,S-9,20190118

Analysis Info

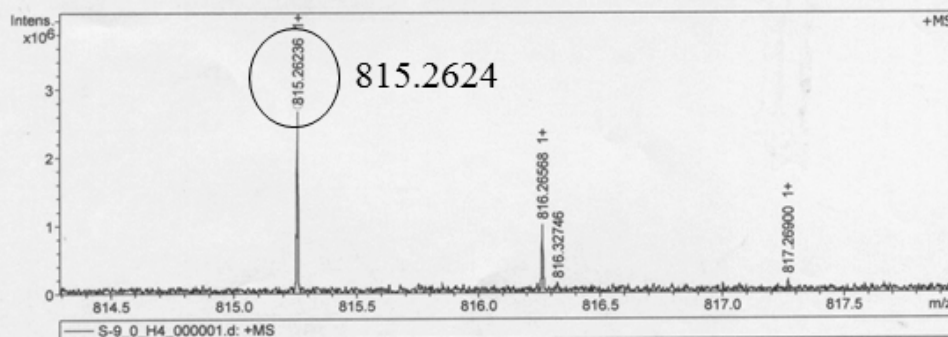
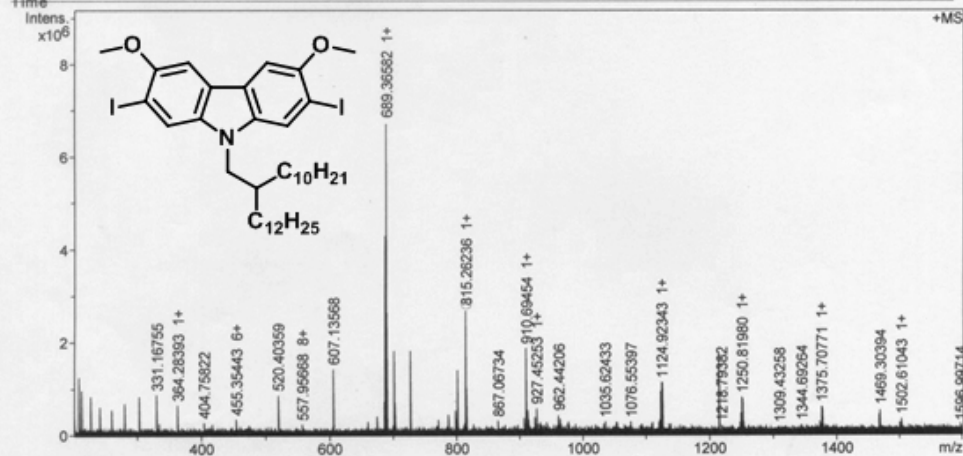
Acquisition D 1/18/2019 4:27:25
RM

Analysis Name D:\Data\MALDI\2019\0118\S-9_0_H4_000001.d
Method MALDI_P_100-3000
Sample Name MURU-N-ESI
Comment

Operator
Instrument solariX

Acquisition Paramet

Acquisition	Mode	Single MS	Acquired	Scans	3	Calibration	Date	Wed Jan 16 05:33:43
Polarity	Positive		No. of Cell	Fills	1	Data Acquisition	2099152	
Broadband	Low Mass	202.1 m/z	No. of Laser	Shots	10	Base Processing	4194304	
Broadband	High	1600.0 m/z	Laser Power		50.4 lp	Ionization	Sine-Bell	
Source		0.001 sec	Laser Shot		0.020 sec		Multiplication	
Accumulation		0.300 sec	Frequency					



Meas. m/z	# Ion	Formula	Score	m/z err	[ppm]	Mean err	[ppm]	mSigma	rdb	e ⁻	Conf	N-Rule
815.262356	1	C38H59I2NO2	100.00	815.262978	0.8			0.8	25.7	9.0	odd	ok

Figure S28. High resolution MALDI-TOF spectra of the a10.

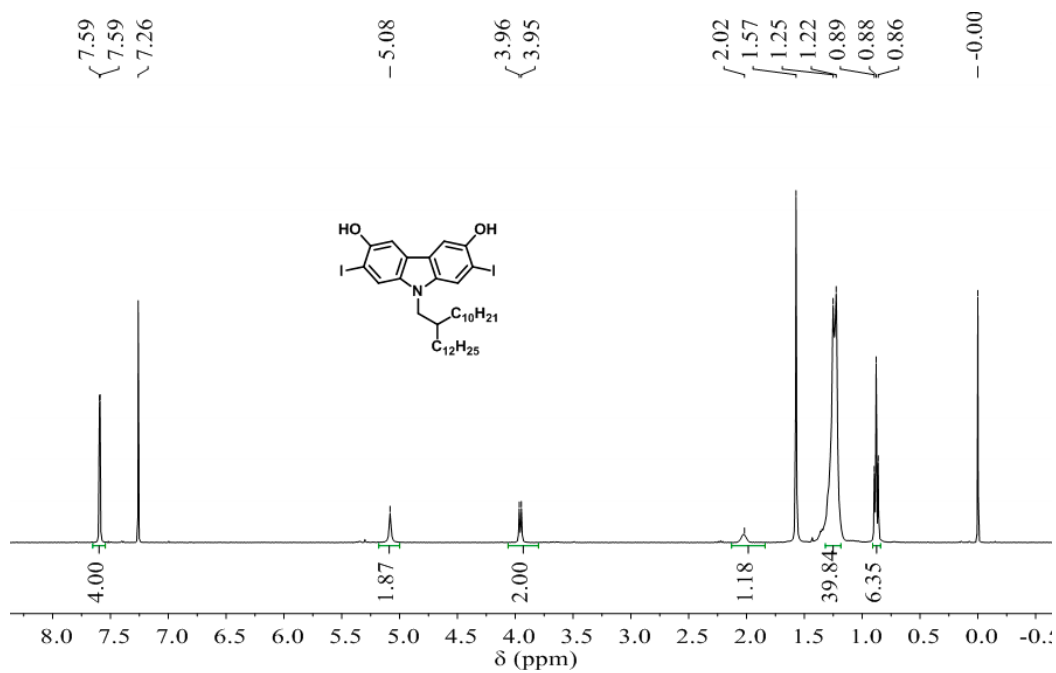


Figure S29. ¹H-NMR of the compound a11 recorded in CDCl₃.

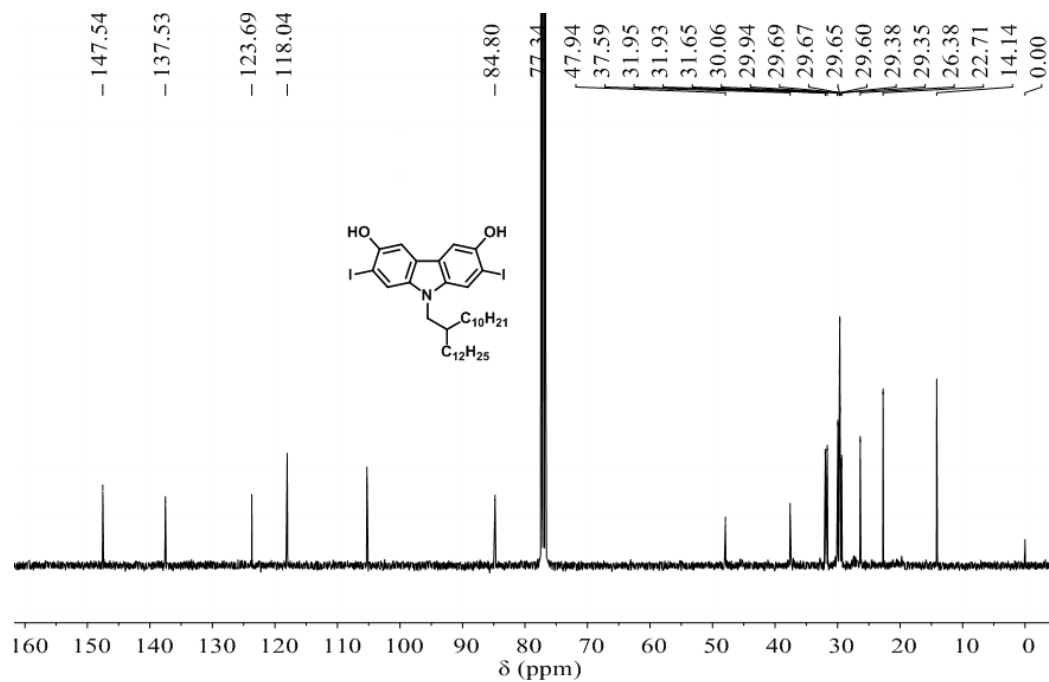


Figure S30. ¹³C-NMR of the compound a11 recorded in CDCl₃.

MALDI,S-10,20190118

Analysis Info

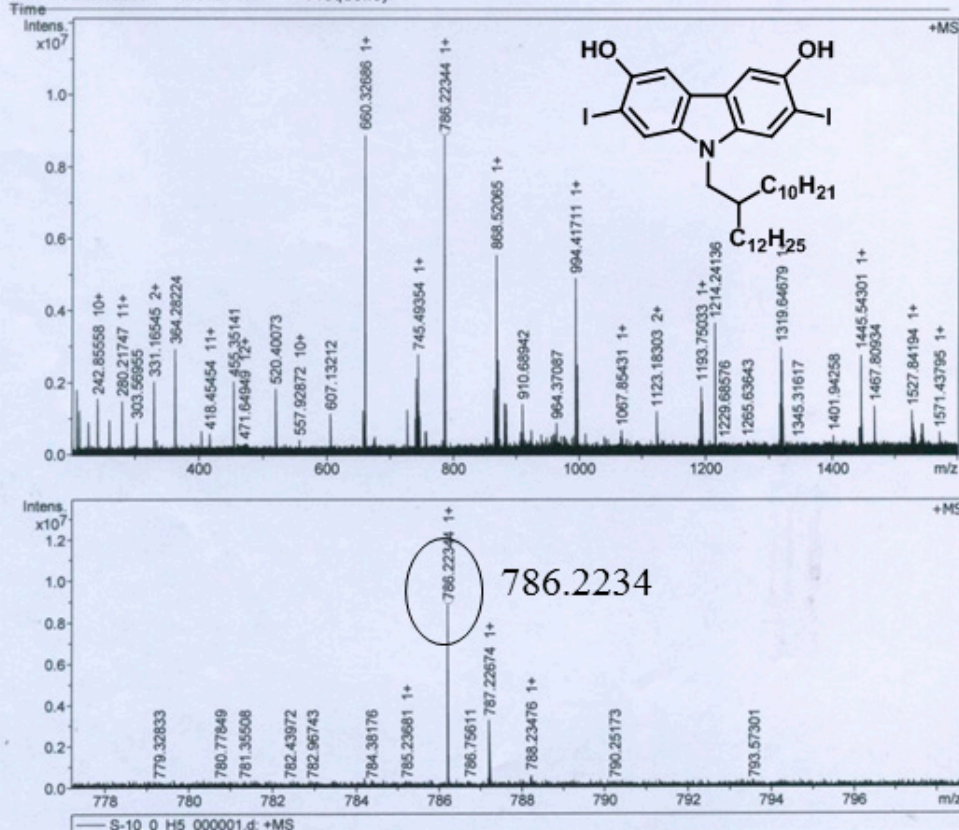
Acquisition D 1/18/2019 4:29:02
RM

Analysis Name D:\Data\MALDI\2019\0118\S-10_H5_000001.d
Method MALDI_P_100-3000
Sample Name MURU-N-ESI
Comment

Operator
Instrument solarix

Acquisition Paramet

Acquisition	Mode	Single MS	Acquired	Scans	11	Calibration	Date	Wed Jan 16 05:33:43
Polarity	Low Mass	Positive	No. of Cell	Fills	1	Data Acquisition	2099152	
Broadband	High	1600.0 m/z	No. of Laser	Shots	10	Base Processing	4194304	
Source		0.001 sec	Laser Power		50.4 lp	Apodization	Sine-Bell	
Accumulation		0.300 sec	Laser Shot		0.020 sec		Multiplication	



Meas. m/z	#	Ion	Formula	Score	m/z err	[ppm]	Mean	err	[ppm]	mSigma	rdB	e ⁻	Conf	N-Rule
786.223439	1	C ₃₆ H ₅₄ I ₂ NO ₂		100.00	786.223852	-0.5				0.5	44.1	9.5	even	ok

Figure S31. High resolution MALDI-TOF spectra of the a11.

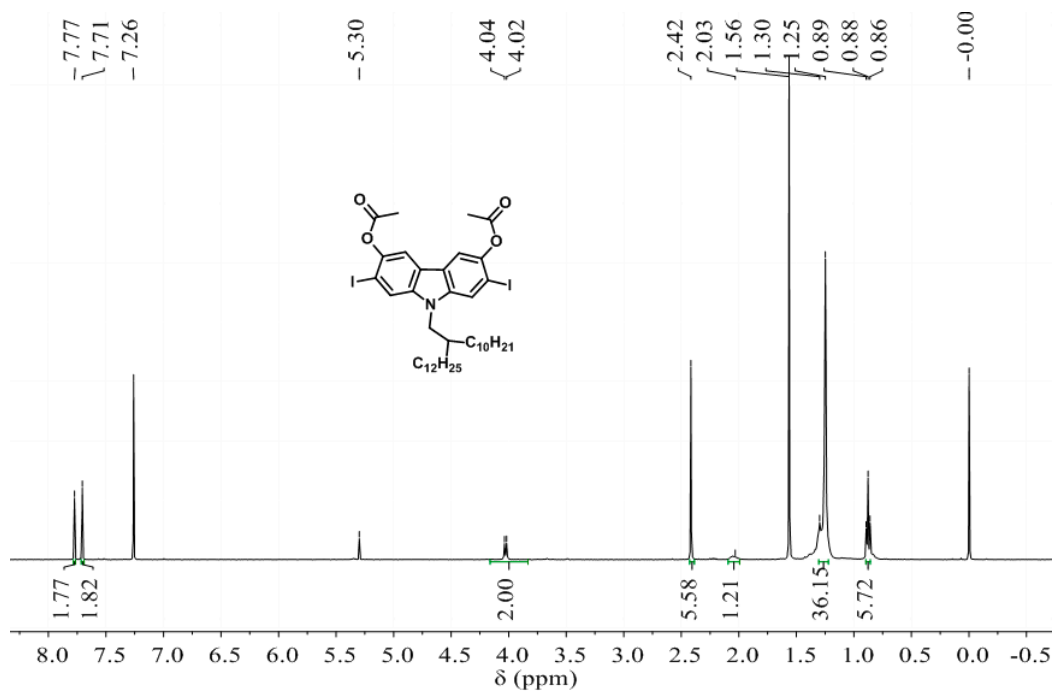


Figure S32. ^1H -NMR of the compound M2 recorded in CDCl_3 .

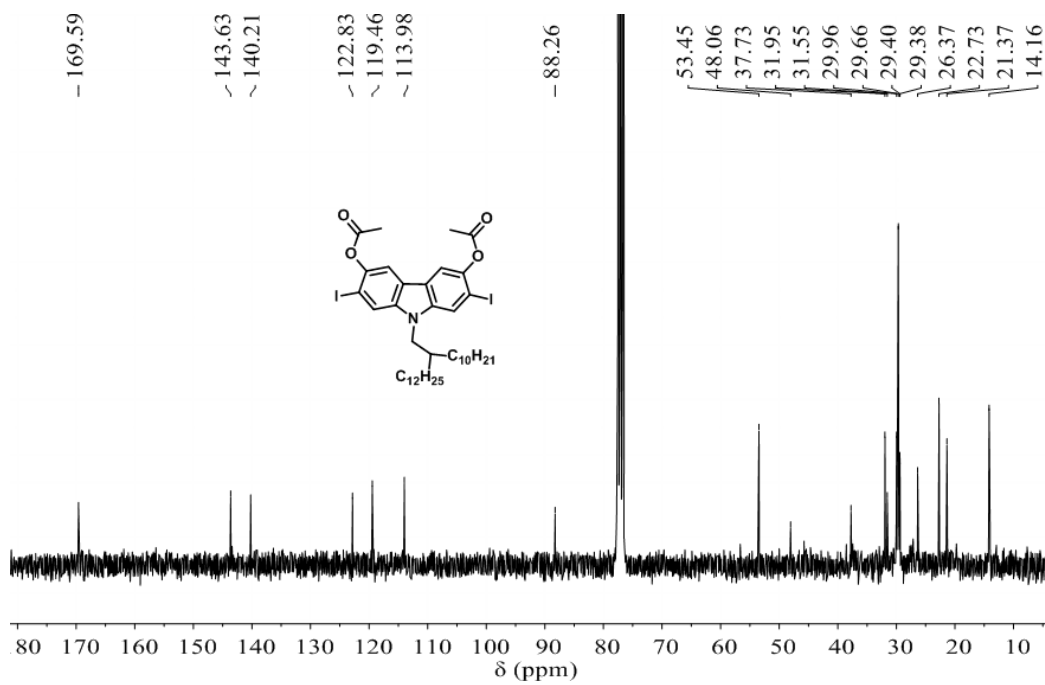


Figure S33. ^{13}C -NMR of the compound M2 recorded in CDCl_3 .

MALDI,S-11,20190118

Analysis Info

Acquisition D1/18/2019 4:37:22
RM

Analysis Name D:\Data\MALDI\2019\0118\S-10_0_H6_000001.d

Method MALDI_P_100-3000

Sample Name MURU-N-ESI

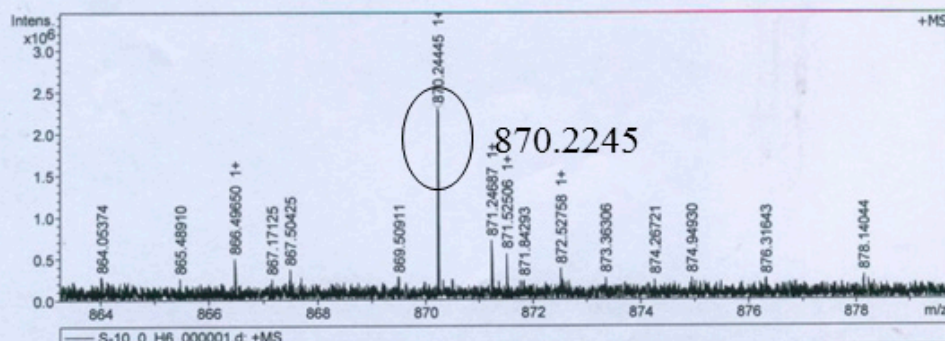
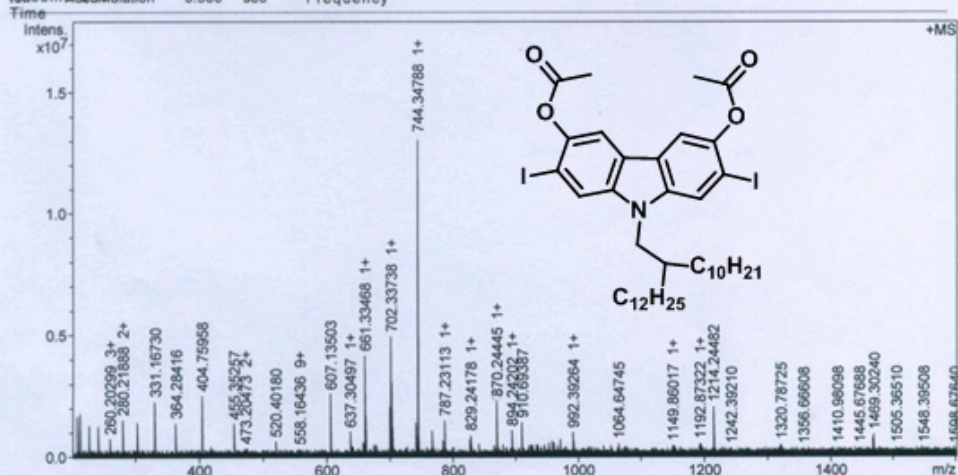
Comment

Operator

Instrument solarix

Acquisition Paramet

Acquisition Mode	Single MS	Acquired Scans	9	Calibration Date	Wed Jan 16 05:33:43
Polarity	Positive	No. of Cell Fills	1	Data Acquisition	20190118
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Base Processing	4194304
Broadband High	1600.0 m/z	Laser Power	65.4 lp	Ionization	Sine-Bell
Reference	0.001 sec	Laser Shot	0.020 sec	Multiplication	
Accumulation	0.300 sec	Frequency			



Meas. m/z	# Ion	Formula	Score	m/z err	[ppm]	Mean err	[ppm]	mSigma	rdb	e ⁻	Conf	N-Rule
870.244450	1	C ₄₀ H ₅₈ I ₂ NO ₄	100.00	870.244982	0.6		0.9	86.4	11.5	even		ok

Figure S34. High resolution MALDI-TOF spectra of the M2.

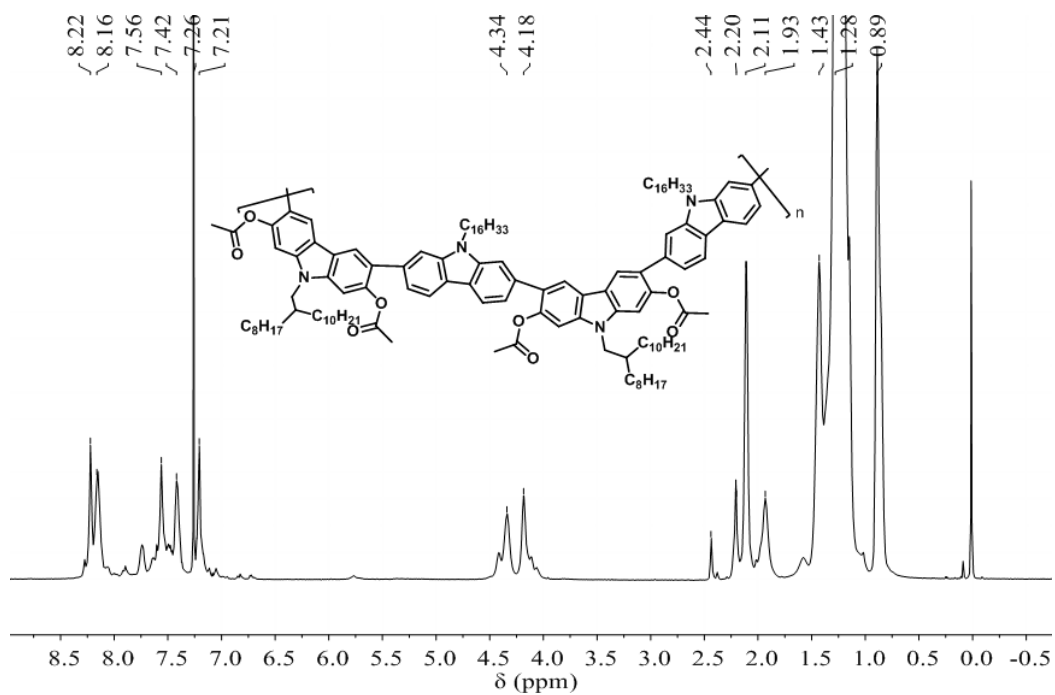


Figure S35. 1H -NMR of the compound P1 recorded in $CDCl_3$.

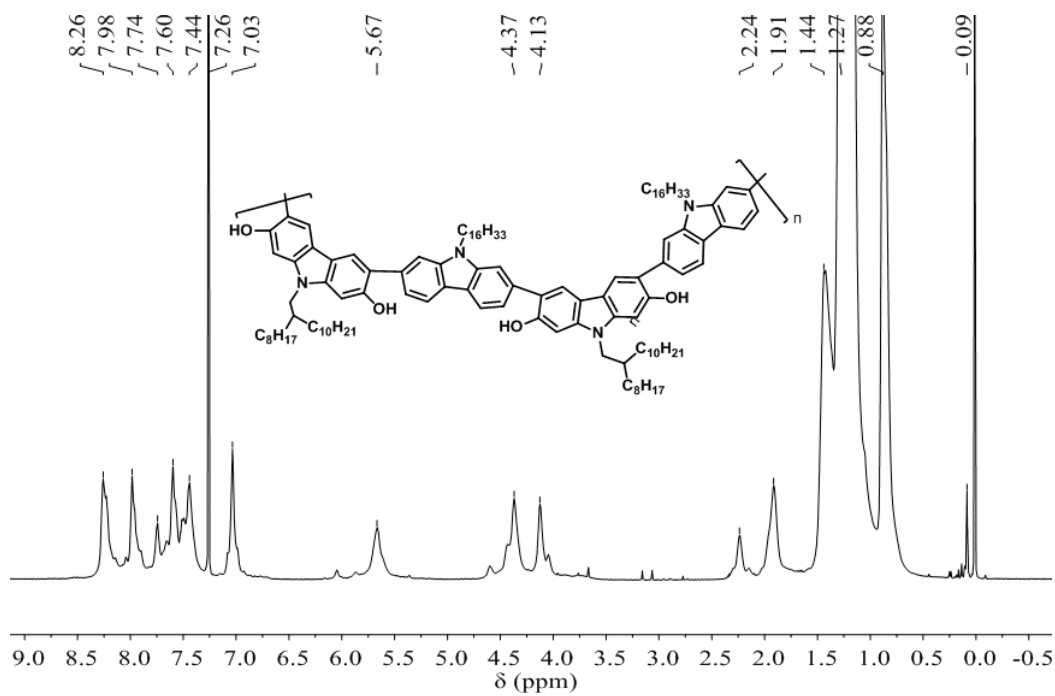


Figure S36. 1H -NMR of the compound P2 recorded in $CDCl_3$.

