# *Electronic Supplementary Information*

# New Pyrido[3,4-b]pyrazine-Based Sensitizers for Efficient and Stable Dye-Sensitized Solar Cells

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# 1. EXPERIMENTAL SECTION

## 1.1. Materials and Instrumentation

### 1.1.1 Materials and reagents

Fluorine-doped $SnO_2$ conducting glass (FTO glass, transmission > 90% in the visible, sheet resistance 15 U/square) was obtained from the Geao Science and Educational Co. Ltd. of China. Acetonitrile, Tetra-n-butyl ammonium hexafluorophosphate ($TBAPF_6$), 4-tert-butylpyridine (4-TBP), and lithium iodide were bought from Fluka and iodine (99.999%) was purchased from Alfa Aesar. Triphenylamine-4-boronic acid was bought from Sun Chemical Technology (Shanghai) Co, Ltd. The starting materials 2,5-dibromo-3,4-diaminopyridine (**1**),[S1] and 4-(bis(4-octoxyphenyl)-amino)-phenylboronic acid [S2] were prepared according to published procedures. All other solvents and chemicals used in this work were of reagent grade and used without further purification.

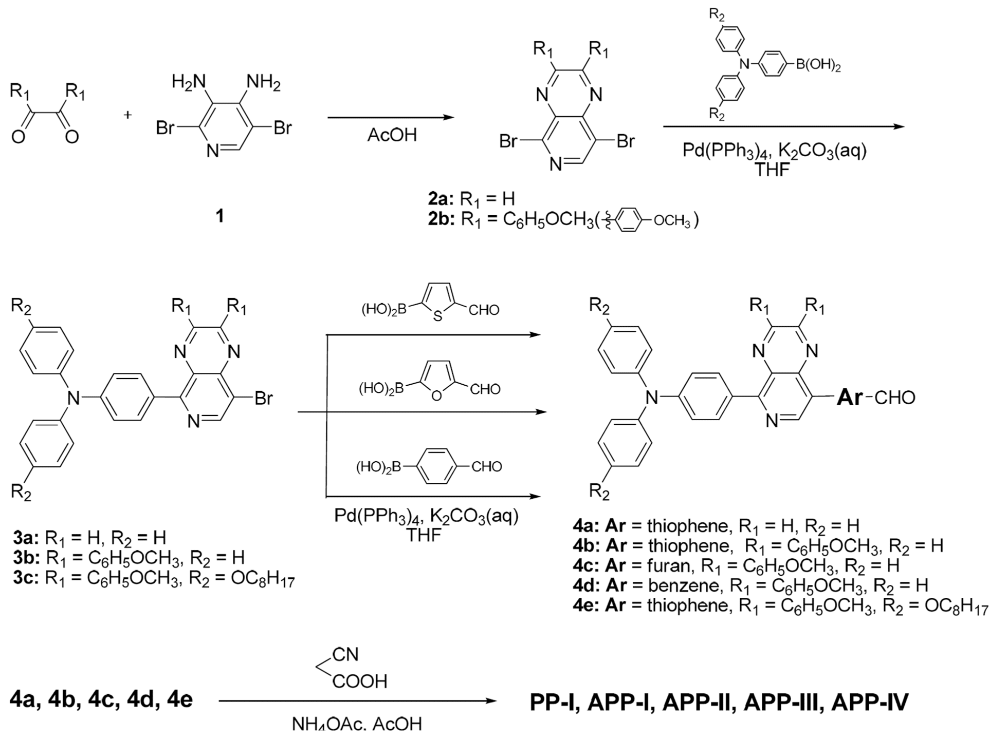
### 1.1.2 Instrumentation:

$^1H$ NMR and $^{13}C$ NMR spectra were obtained with a Brücker AM 400 spectrometer. Mass spectra were measured with an ESI mass spectrometer. The UV–Vis spectra were measured with a Varian Cary 500 spectrophotometer. The cyclic voltammograms of dyes were obtained with a Versastat II electrochemical workstation (Princeton applied research) using a normal three-electrode cell with a Pt working electrode, a Pt wire counter electrode, and a regular calomel reference electrode in saturated KCl solution.

The setup used for standard photovoltaic characterization (*J*-*V* curve) consists of a

450 W xenon lamp (Oriel), whose spectral output was matched in the region of 350–750 nm with the aid of a Schott K113 Tempax sunlight filter (PräzisionsGlas & Optik GmbH), and a source meter (Keithley 2400) to apply potential bias and measure the photogenerated current. A set of metal-mesh filters was used to adjust the light intensity to a desired level. IPCE was measured using a SR830 lockin amplifier, however the incident light (300 W xenon lamp, ILC Technology) was focused through a Gemini-180 double monochromator (Jobin-Yvon Ltd.). The cells were measured with an external light bias (100 W/m$^2$ intensity) provided by LED array. A black metal mask defined the cell active area to be 0.159 cm$^2$.

## 1.2. Synthesis



**Scheme S1** Synthesis of PP-based dyes

### 1.2.1 Synthesis of PP-based dyes

**5,8-dibromopyrido[3,4-b]pyrazine (2a).** To a mixture of 2,5-dibromo-3,4-diaminopyridine (**1**) (1.068 g, 4 mmol) in acetic acid (20 mL) in a 50 mL flask, was added glyoxal (290 mg, 5 mmol) dropwise. The reaction mixture was heated for 5 hours at 80 °C and then poured into water after cooling to the room temperature. The precipitate was filtered and washed with water. The residue was purified by flash chromatography with using $CH_2Cl_2$ (dichloromethane): PE (petroleum ether) = 1/2 (v/v) as eluent to give 800 mg of pale yellow solid. (Yield: 70%).$^1$H-NMR (400 MHz, $CDCl_3$, ppm): δ = 9.19 (d, *J* = 1.7 Hz, 1 H), 9.12 (d, *J* = 1.7 Hz, 1 H), 8.85 (s, 1 H); $^{13}$C NMR(100 MHz, $CDCl_3$, ppm): 150.1, 147.8, 147.7, 146.8, 144.7, 138.1, 120.5; HRMS (ESI, m/z): $[M+H]^+$ calcd for ($C_7H_4N_3Br_2$), 287.8771; found, 287.8772.

**5,8-dibromo-2,3-bis(4-methoxyphenyl)pyrido[3,4-b]pyrazine (2b).** A procedure similar to that for **2a** but with 4,4'-dimethoxybenzil instead of glyoxal giving **2b** as a yellow solid (yield: 61%). $^1$H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.61 (s, 1 H), 7.63-7.58 (m, 4 H), 6.90-6.81 (m, 4 H), 3.80-3.78 (m, 6 H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): δ = 161.6, 161.3, 157.6, 155.5, 146.7, 145.8, 142.2, 135.6, 131.7, 129.9, 129.7, 120.0, 114.1, 55.4; HRMS (ESI, m/z): $[M+H]^+$ calcd for ($C_{21}H_{16}N_3O_2Br_2$), 499.9609; found, 499.9604.

**4-(8-bromopyrido[3,4-b]pyrazine)-N,N'-bisphenyl aniline (3a).** A mixture of compound **2a** (287 mg, 1 mmol), 4-(bisphenylamino)phenyl bronic acid (289 mg, 1 mmol), Pd ($PPh_3$)$_4$ (15 mg) and 2 M $K_2CO_3$ (aq, 5 mL) in 15 mL of THF was heated to 80 °C under $N_2$ for 12 h. After cooling to room temperature, the mixture was poured into water and extracted with $CH_2Cl_2$ (3×10 mL). The combined organic layers were washed with brine and water and dried with anhydrous $MgSO_4$. The solvent was evaporated, and the residue was purified by flash chromatography with ($CH_2Cl_2$/ PE = 1/2-1/1, v/v) to give an orange solid (300 mg). Yield: 66%. $^1$H-NMR (400 MHz, $CDCl_3$, ppm): δ = 9.03 (d, *J* = 4 Hz, 1 H), 8.96 (d, *J* = 4 Hz, 1 H), 8.93 (s, 1 H), 8.08 (d, *J* = 8 Hz, 2 H), 7.31-7.29 (m, 4 H), 7.21-7.19 (m, 6 H), 7.08-7.05 (m, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): δ = 158.8, 149.1, 147.9, 147.4, 146.1, 145.0, 144.1, 131.6, 129.4, 128.1, 125.2, 123.4, 122.5, 122.0; HRMS (ESI, m/z): $[M+H]^+$ calcd for ($C_{25}H_{18}N_4Br$), 453.1846; found, 453.1840.

**4-(8-bromo-2,3-bis(4-methoxyphenyl)pyrido[3,4-b]pyrazine)-N,N’-bisphenyl aniline (3b).** The synthesis method resembles that of compound **3a** and the compound was purified by flash chromatography with ($CH_2Cl_2$/ PE = 1/2-1/1, v/v) to give an orange solid (yield: 75%). $^1$H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.96 (s, 1 H), 8.21 (d, *J* = 8 Hz, 2 H), 7.73 (d, *J* = 12 Hz, 2 H), 7.57 (d, *J* = 8 Hz, 2 H), 7.32-7.28 (m, 4 H), 7.21-7.19 (m, 6 H), 7.10-7.07 (m, 2 H), 6.91 (d, *J* = 8 Hz, 2 H), 6.87 (d, *J* = 8 Hz, 2 H), 3.86 (s, 3 H), 3.84 (s, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): δ = 161.3, 160.8, 149.3, 147.5, 147.3, 132.3, 131.4, 130.7, 130.3, 125.2, 123.6, 121.9, 114.0, 55.37, 30.0; HRMS (ESI, m/z): $[M+H]^+$ calcd for ($C_{39}H_{30}N_4O_2Br$), 665.1552; found, 665.1550.

**4-(8-bromo-2,3-bis(4-methoxyphenyl)pyrido[3,4-b]pyrazine)-N,N’-bis(4-octoxyphenyl)) aniline (3c).** The synthesis method resembles that of compound **3a** and the compound was purified by flash chromatography with ($CH_2Cl_2$/PE= 1/2-1/1, v/v) to give a red solid. Yield: 76%. $^1$H-NMR (400 MHz, $CDCl_3$, ppm): δ = 8.92 (d, *J* = 8 Hz, 1H), 8.17 (d, *J* = 8 Hz, 2 H), 7.71 (d, *J* = 8 Hz, 2H), 7.54 (d, *J* = 8 Hz, 2 H),7.14-7.11 (m, 4 H), 7.02 (d, *J* = 8 Hz, 2 H), 6.88-6.84 (m, 8 H), 3.96-3.93 (m, 4 H), 3.84-3.82 (m, 6 H), 1.80-1.75 (m, 4 H), 1.47-1.43 (m, 4 H), 1.32-1.23 (m, 16 H), 0.91-0.84 (m, 6 H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): δ =154.75, 143.5, 138.7, 131.2, 130.7, 128.9, 126.4, 123.3, 117.8, 114.4, 114.1, 67.3, 30.7, 28.7, 26.2, 25.1, 21.5, 13.1; HRMS (ESI, m/z): $[M+H]^+$ calcd for ($C_{55}H_{62}N_4O_4Br$), 921.3954; found, 921.3953.

**5-(8-(4-(diphenylamino)phenyl)-pyrido[3,4-b]pyrazine)-thiophene-2-carbaldehyde (4a).** A mixture of compound **3a** (226 mg, 0.5 mmol), 5-formylthiophen-2-yl boronic acid (100 mg, 0.6 mmol), $Pd(PPh_3)_4$ (15 mg) and 2 M $K_2CO_3$ (aq, 5 mL) in 15 mL of THF was heated to 80 °C under $N_2$ for 12 h. After cooling to room temperature, the mixture was poured into water and extracted with $CH_2Cl_2$ (3×10 mL). The combined organic layers were washed with brine and water and dried with anhydrous $MgSO_4$. The solvent was evaporated, and the residue was purified by flash chromatography with ($CH_2Cl_2$/PE = 1/1, v/v) to give a red solid (180 mg). Yield: 74%. $^1$H-NMR (400 MHz, $CDCl_3$, ppm): δ = 10.01 (s, 1 H), 9.30(s, 1 H), 9.12 (d, *J* = 1.7 Hz, 1 H), 9.06 (d, *J* = 1.7 Hz, 1 H), 8.15 (d, *J* = 8 Hz, 2 H), 7.95 (d, *J* = 4 Hz, 1 H), 7.86 (d, *J* = 4 Hz, 1 H), 7.33-7.29 (m, 4 H), 7.23-7,21 (m, 6 H), 7.12-7.10 (m, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): δ = 183.4, 160.0, 147.1, 145.5, 145.4, 145.3, 144.8, 135.9, 132.4, 130.0, 129.5, 127.5, 125.5, 123.9, 123.6, 121.4; HRMS (ESI, m/z): $[M+H]^+$ calcd for ($C_{30}H_{21}N_4O_3$), 485.1614; found, 485.1452.

**5-(8-(4-(diphenylamino)phenyl)-2,3-bis(4-methoxyphenyl)pyrido[3,4-b]pyrazine)-thiophene-2-carbaldehyde (4b).** The synthesis method resembles that of compound **4a** and the compound was purified by flash chromatography with ($CH_2Cl_2$/PE = 1/1, v/v) to give a red solid. Yield: 91%. $^1$H-NMR (400 MHz, $CDCl_3$, ppm): δ = 10.01 (s, 1 H), 9.23 (s, 1 H), 8.32(d, *J* = 12 Hz, 2 H), 7.95(d, *J* = 4 Hz, 1 H), 7.86 (d, *J* = 4 Hz, 1 H), 7.79-7.76 (m, 2 H), 7.62-7.60 (m, 2 H), 7.34-7.30 (m, 4 H), 7.23-7.21 (m, 6 H), 7.12-7.08 (m, 2 H), 6.96 (d, *J* = 8 Hz, 2 H), 6.89 (d, *J* = 12 Hz, 2 H), 3.88 (s, 3 H), 3.84 (s, 3 H); $^{13}$C NMR(100 MHz, $CDCl_3$, ppm): δ = 183.4, 161.3, 160.8, 158.2, 155.1, 152.9, 149.5, 147.3, 146.2, 145.1, 144.2, 140.1, 136.1, 132.5, 132.0, 131.4, 130.1, 130.2, 126.6, 125.4, 123.7, 122.8, 121.7, 114.1, 55.4; HRMS (ESI, m/z): $[M+H]^+$ calcd for ($C_{44}H_{33}N_4O_3S$), 697.2273; found, 697.2275.

**5-(8-(4-(diphenylamino)phenyl)-2,3-bis(4-methoxyphenyl)pyrido[3,4-b]pyrazine)-furan-2-carbaldehyde (4c).** The synthesis method resembles that of compound **4a** and the compound was purified by flash chromatography with ($CH_2Cl_2$/PE = 1/1, v/v) to give a red solid. Yield: 71%. $^1$H-NMR (400 MHz, $CDCl_3$, ppm): δ = 9.78 (s, 1 H), 9.45(s, 1 H), 8.32(d, *J* = 8 Hz, 2 H), 7.98(d, *J* = 4 Hz, 1 H), 7.67(d, *J* = 8 Hz, 2 H), 7.58 (d, *J* = 8 Hz, 2 H), 7.46(d, *J* = 4 Hz, 1 H), 7.33-7.29 (m, 4 H), 7.22-7.20 (m, 6H), 7.12-7.08 (m, 2 H), 6.95 (d, *J* = 8 Hz, 2 H), 6.88 (d, *J* = 8 Hz, 2 H), 3.88 (s, 3 H), 3.84 (s, 3 H); $^{13}$C NMR(100 MHz, $CDCl_3$, ppm): δ = 177.7, 161.0, 147. 3, 144.2, 141.7, 140.8, 131.3, 123.6, 122.7, 118.2, 116.1, 114.0, 53.7; HRMS (ESI, m/z): $[M+H]^+$ calcd for ($C_{44}H_{33}N_4O_4$), 681.2502; found, 681.2501.

**4-(8-(4-(diphenylamino)phenyl)-2,3-bis(4-methoxyphenyl)pyrido[3,4-b]pyrazi**

**ne)-benaldehyde (4d).** The synthesis method resembles that of compound **4a** and the compound was purified by flash chromatography with ($CH_2Cl_2$/PE = 1/1, v/v) to give an orange solid. Yield: 80%. $^1$H-NMR (400 MHz, $CDCl_3$, ppm): δ = 10.14 (s, 1 H), 8.90 (s, 1 H), 8.29 (d, *J* = 8 Hz, 2 H), 8.07 (m, 4 H), 7.62-7.59 (m, 4 H), 7.33-7.29 (m, 4 H), 7.23-7.21 (m, 6 H), 7.11-7.08 (m, 2 H), 6.89-6.85 (m, 4 H), 3.84 (s, 3 H), 3.83 (s, 3 H); $^{13}$C NMR(100 MHz, $CDCl_3$, ppm): δ = 192.2, 161.1, 160.7, 158.6, 154.9, 152.4, 149.3, 145.8, 144.4, 141.6, 138.7, 135.5, 133.0, 131.1, 129.5, 124.2, 123.6, 121.9, 114.0, 55.4, 30.3; HRMS (ESI, m/z): $[M+H]^+$ calcd for ($C_{46}H_{35}N_4O_3$), 691.2709; found, 691.2712.

**5-(8-(4-(bis(4-octyloxyphenyl)amino)phenyl)-2,3-bis(4-methoxyphenyl)pyrido[3,4-b]pyrazine)-thiophene-2-carbaldehyde (4e).** The synthesis method resembles that of compound **4a** and the compound was purified by flash chromatography with ($CH_2Cl_2$/PE = 1/1, v/v) to give a red solid. Yield: 82%. $^1$H-NMR (400 MHz, $CDCl_3$, ppm): δ = 9.94 (s, 1 H), 9.15 (s, 1 H), 8.21 (d, *J* = 8 Hz, 2 H), 7.87 (d, *J* = 4 Hz, 1 H), 7.78 (d, *J* = 1.7 Hz, 1 H), 7.70 (d, *J* = 8 Hz, 2 H), 7.53 (d, *J* = 8 Hz, 2 H), 7.08 (d, *J* = 8 Hz, 4 H), 6.98 (d, *J* = 8 Hz, 2 H), 6.88 (d, *J* = 8 Hz, 2 H), 6.83-6.79(m, 6 H), 3.90-3.87 (m, 4 H), 3.81-3.78 (m, 6 H), 1.74-1.69 (m, 4 H), 1.40-1.25 (m, 4 H), 1.23-1.20 (m, 16 H), 0.84-0.79 (m, 6 H); $^{13}$C NMR(100 MHz, $CDCl_3$, ppm): δ = 184.0, 161.0, 158.0, 156.0, 153.2, 150.2, 147.5, 141.8, 140.2, 134.7, 131.4, 130.8, 127.8, 118.8, 116.7, 115.4, 114.0, 68.3, 55.4, 31.8, 29.7, 26.1, 22.7, 14.2; HRMS (ESI, m/z): $[M+H]^+$ calcd for ($C_{60}H_{65}N_4O_5S$), 953.4676; found, 953.4680.

**2-cyano-3-(5-(8-(4-(diphenylamino)phenyl)-pyrido[3,4-b]pyrazine)-thiophene-**

**2-yl-)acrylic acid (PP-I).** To a stirred solution of compound **4a** (121 mg, 0.25 mmol) and cyanoacetic acid (85 mg, 1 mmol) in acetic acid (10 mL) was added ammonium acetate (120 mg). The reaction mixture was heated to reflux under $N_2$ for 12 h. After cooling to room temperature, the mixture was poured into the water (200 mL). The precipitate was filtered and washed with brine and water. The residue was purified by flash chromatography with (ethanol/$CH_2Cl_2$ = 1/10, v/v) to yield 88 mg of red solid. Yield: 64%. $^1$H-NMR (400 MHz, DMSO-$d_6$, ppm): $\delta$ = 9.45 (s, 1H), 9.24 (s, 1H), 9.15 (s, 1H), 8.34 (s, 1H), 8.19 (s, 1H), 8.14 (d, $J$ = 8 Hz, 2 H), 7.95 (s, 1 H), 7.40-7.36 (m, 4 H), 7.18-7.12 (m, 6 H), 7.04 (d, $J$ = 8 Hz, 2 H); $^{13}$C NMR (100 MHz, DMSO-$d_6$, ppm): $\delta$ = 163.9, 157.7, 148.6, 146.0, 144.2, 143.6, 142.2, 141.5, 139.4, 135.0, 132.5, 129.7, 125.0, 124.0, 123.0, 120.48. HRMS (ESI, m/z): $[M+H]^+$ calcd for ($C_{33}H_{22}N_5O_2S$), 552.1494; found, 552.1489.

**2-cyano-3-(5-(8-(4-(diphenylamino)phenyl)-2,3-bis(4-methoxyphenyl)pyrido[3,4-b]pyrazine)-thiophene-2-yl-)acrylic acid (APP-I).** The synthesis method resembles that of compound **PP-I** and the compound was purified by flash chromatography with (ethanol/$CH_2Cl_2$ = 1/10, v/v) to give a red solid. Yield: 87%. $^1$H-NMR (400 MHz, DMSO-$d_6$, ppm): $\delta$ = 9.49 (s, 1 H), 8.50 (s, 1 H), 8.36 (d, $J$ = 8 Hz, 2 H), 8.28 (d, $J$ = 4 Hz, 1 H), 8.03 (d, $J$ = 8 Hz, 1 H), 7.65 (d, $J$ = 8 Hz, 2 H), 7.60 (d, $J$ = 8 Hz, 2 H), 7.41-7.37 (m, 4 H), 7.17-7.14 (m, 6 H), 7.09 (d, $J$ = 8 Hz, 2 H), 7.00-6.96 (m, 4 H), 3.81-3.79 (m, 6 H); $^{13}$C NMR (100 MHz, DMSO-$d_6$, ppm): $\delta$ = 159.7, 148.5, 146.7, 144.9, 142.6, 141.1, 139.0, 136.3, 132.4, 129.8, 125.2, 123.9, 122.3, 121.9, 55.2, 33.2; HRMS (m/z): $[M-H]^-$ calcd. for ($C_{47}H_{32}N_5O_4S$): 762.2175;

found: 762.2177.

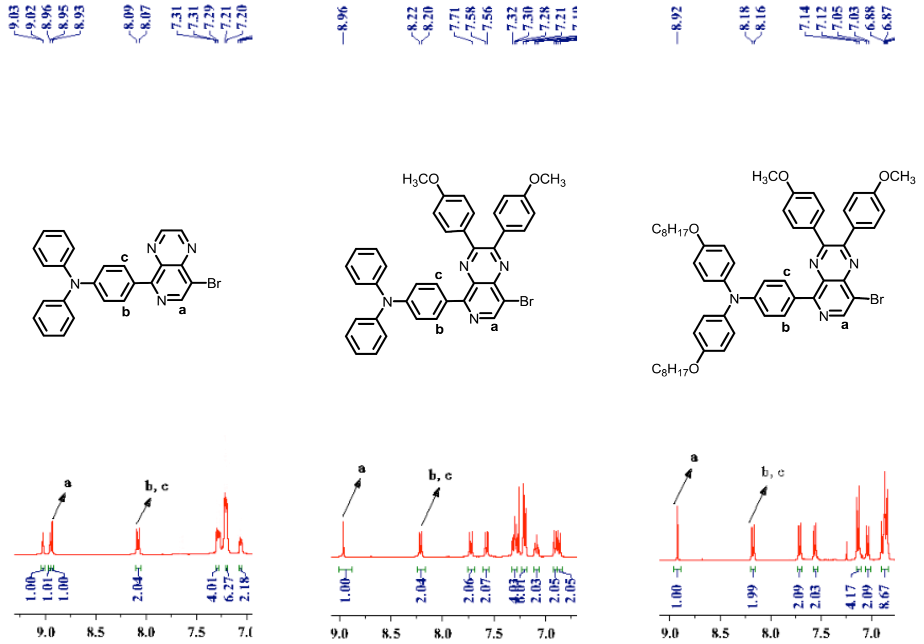
**2-cyano-3-(5-(8-(4-(diphenylamino)phenyl)-2,3-bis(4-methoxyphenyl)pyrido[3,4-b]pyrazine)-furan-2-yl-)acrylic acid (APP-II).** The synthesis method resembles that of compound **PP-I** and the compound was purified by flash chromatography with (ethanol/$CH_2Cl_2$ = 1/10, v/v) to give a red solid. Yield: 88%. $^1$H-NMR (400 MHz, DMSO-*d*$_6$, ppm): δ = 9.15 (s, 1 H), 8.24-8.21 (m, 2 H), 7.90 (s, 1 H), 7.75 (s, 1 H), 7.41-7.34 (m, 6 H), 7.26 (s, 1 H), 7.15-7.11 (m, 4 H), 7.07 (d, *J* = 4 Hz, 4 H), 6.97-6.93 (m, 4 H), 6.77(d, *J* = 8 Hz, 2 H), 3.78-3.74 (m, 6 H); $^{13}$C NMR (100 MHz, DMSO-*d*$_6$, ppm): δ = 160.2, 146.7, 144.6, 140.1, 138.3, 132.5, 131.4, 129.6, 127.2, 125.1, 124.6, 120.1, 114.5, 55.3, 28.7; HRMS (m/z): $[M+H]^+$ calcd. for ($C_{47}H_{34}N_5O_5$): 748.2560; found: 748.2557.

**2-cyano-3-(5-(8-(4-(diphenylamino)phenyl)-2,3-bis(4-methoxyphenyl)pyrido[3,4-b]pyrazine)-phenyl)acrylic acid (APP-III).** The synthesis method resembles that of compound **PP-I** and the compound was purified by flash chromatography with (ethanol/$CH_2Cl_2$ = 1/10, v/v) to give a red solid. Yield: 83%. $^1$H-NMR (400 MHz, DMSO-*d*$_6$, ppm): δ = 8.84 (s, 1 H), 8.29(s, 1 H), 8.25 (d, *J* = 8 Hz, 2 H), 8.10 (d, *J* = 8 Hz, 2 H), 8.01 (d, *J* = 8 Hz, 2 H), 7.54-7.51 (m, 4 H), 7.39-7.35 (m, 4 H), 7.15-7.12 (m, 6 H), 7.06 (d, *J* = 8 Hz, 2 H), 6.94-6.90 (m, 4 H), 3.77-3.76 (m, 6 H); $^{13}$C NMR (100 MHz, DMSO-*d*$_6$, ppm): δ = 160.6, 156.7, 155.0, 151.9, 148.5, 146.7, 140.8, 132.1, 130.2, 129.2, 124.9, 123.6, 120.7, 113.8, 55.2, 28.9; HRMS (m/z): $[M-H]^-$ calcd. for ($C_{49}H_{34}N_5O_4$): 756.2611; found: 756.2618.

**2-cyano-3-(5-(8-(4-bis(4-octyloxyphenyl)amino)phenyl)-2,3-bis(4-methoxyphen**

**yl)pyrido[3,4-b]pyrazine)-thiophene-2-yl-)acrylic acid (APP-IV).** The synthesis method resembles that of compound **PP-I** and the compound was purified by flash chromatography with (ethanol/$CH_2Cl_2$ = 1/10, v/v) to give a red solid. Yield: 85%. $^1$H-NMR (400 MHz, DMSO-$d_6$, ppm): $\delta$ = 9.33 (s, 1 H), 8.43 (s, 1 H), 8.28 (d, $J$ = 8 Hz, 2 H), 8.13 (d, $J$ = 4 Hz, 1 H), 7.95 (d, $J$ = 4 Hz, 1 H), 7.70 (d, $J$ = 8 Hz, 2 H), 7.35-7.20 (m, 4 H), 7.18-7.06 (m, 6 H), 6.96 (d, $J$ = 8 Hz, 2 H), 6.90-6.84 (m, 4 H), 3.98-3.92 (m, 4 H), 3.82-3.76 (m, 6 H), 1.70-1.66 (m, 4 H), 1.37-1.24(m, 20 H), 0.88-0.83(m, 6 H); $^{13}$C NMR (100 MHz, DMSO-$d_6$, ppm): $\delta$ = 163.5, 154.7, 153.6, 149.5, 147.0, 146.8, 135.9, 132.1, 129.5, 123.6, 115.7, 110.3, 55.4, 31.2, 28.9, 28.6, 25.5, 22.1, 13.9; HRMS (ESI, m/z): $[M+H]^+$ calcd for ($C_{63}H_{66}N_5O_6S$), 1020.4734; found, 1020.4730.

## 1.2.2



Compound **3a** Compound **3b** Compound **3c**

**Figure S1** $^1$H NMR spectrum of compound **3a-3c** in $CDCl_3$ ($\delta$ = 7.27 ppm).

### 1.3. Electrochemical properties

CV curves were recorded in $CH_2Cl_2$ solution with 0.1 M tetra-n-butylammonium hexafluorophosphate ($TBAPF_6$) as electrolyte with a three-electrode system (working electrode: Pt; reference electrode: SCE; calibrated with ferrocene/ferrocenium ($Fc/Fc^+$) as an external reference. Counter electrode: Pt). Figure S2 shows the cyclic voltammograms of **PP-I**, **APP-I~IV**.

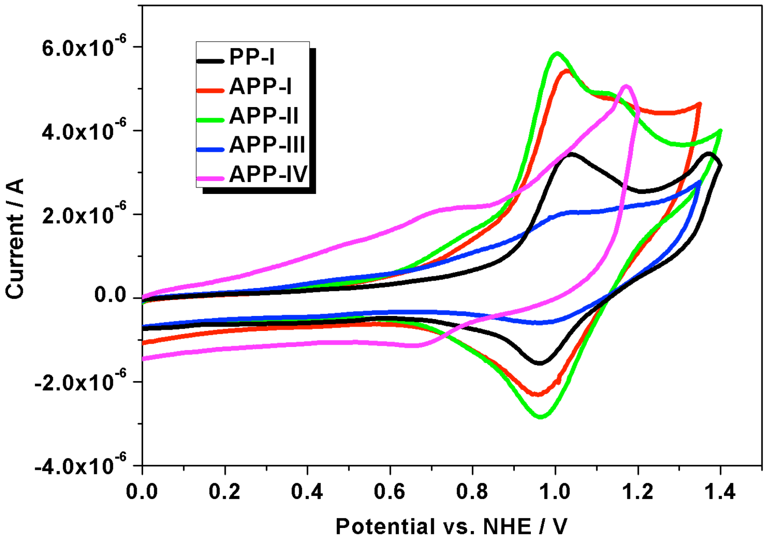


**Figure S2.** Cyclic Voltammetry of **PP-I**, **APP-I~IV**

### 1.4. Theoretical approach

Alternating the π-bridges and the PP-cores leads to differences in the orbital energies and the electron density distribution of the dyes. As seen from the orbital representation of **PP-I** in Figure 4, the thiophene spacer allows for a complete conjugation of the HOMO from the triarylamine to the cyanoacrylic acid. The HOMO is energetically isolated by almost 1 eV from the lower HOMO orbitals allowing the assumption that charge transfer transitions from the HOMO to LUMO and to higher LUMO orbitals will dominate the excited state features of these dyes. LUMO and LUMO+1 coefficients are found extending throughout the PP-core to the anchoring moieties, which may give rise to low-energy ICT transitions from donor to acceptor. Former results from TD-DFT calculations on similar quinoxaline-based D-A-π-A sensitizers support these assumptions very well. There, the authors confirm that the lowest energy excited state transitions transfer electron density to the LUMO and LUMO+1 orbitals, which strongly overlap with the anchoring groups.[S3] Importantly, the LUMO+2 is solely localized on the PP-unit, which corroborates its electron accepting features. However, an energy gap of more than 1 eV separates the LUMO+2 from the LUMO+1, which proposes that clean triarylamine to PP excitations are higher in energy. More plausible is that the low-energy excitations from HOMO to LUMO and LUMO+1 will exhibit a mixed donor to PP-core and donor to cyanoacrylic acid transition character. This is in line with the overlap of the two main absorptions in Figure 2. Considering **APP-I**, **APP-II** and **APP-III** suggests that modifying the PP-core only slightly enhances the delocalization of the electron density. The HOMOs remain nearly unaffected, except in **APP-III**, where the dihedral angle of the phenyl spacer implies a disruption of π-conjugation and a stronger localization of the electron density on the triarylamine. This effect in an increase of the HOMO-LUMO energy gap by ~ 0.1 eV as compared with **APP-I** and **APP-II** and is reflected by the blue-shifted absorption of **APP-III** in Figure 2. This electronic decoupling of the donor and acceptor moiety is further envisioned by firstly the redistribution of the HOMO-2 orbital, which becomes the HOMO-1 in **APP-III** and secondly an enhanced localization of the LUMO. Another effect of modifying the π-bridge is seen when considering the PP-acceptor state. In **APP-I** the LUMO+3 is entirely localized on the PP-core, whereas in **APP-II** and **APP-III** the same state is the energetically lower LUMO+2. Finally, as seen from the orbital representations of **APP-IV**, attaching the octyloxy groups significantly extends the π-conjugation of the donor, which in particular raises the HOMO energies and facilitates their oxidation. As a consequence, the HOMO-LUMO gap of **APP-IV** decreases to a value of 2.08 eV, which is the lowest energy among the investigated dyes and corresponds well with the red-shift in the absorption spectra (Figure 2).

**Laser studies:** The nanosecond laser flash photolysis technique was applied to the dye-sensitized, 4 μm thick, transparent $TiO_2$ mesoporous films deposited on normal flint glass. The samples were excited by pulses produced at a repetition rate of 30 Hz by a broad-band optical parametric oscillator (GWU OPO-355) pumped by a Powerlite 7030 frequency-tripled Q-switched Nd:YAG laser (Continuum, Santa Clara, California, USA). The output excitation wavelength was tuned at $\lambda_{exc}$ = 530 nm with a pulse width of 7 ns (fwhm). The laser beam was expanded by a planoconcave lens to irradiate a large cross-section of the sample, whose surface was kept at a 45 degree angle to the excitation beam. The laser fluence on the sample was kept at a low level (30 μJ $cm^{-2}$ per pulse) to ensure that, on average, less than one electron is injected per nanocrystalline $TiO_2$ particle upon pulsed irradiation. The probe light, produced by a continuous wave xenon arc lamp, was first passed through a monochromator tuned in

20 nm steps throughout the 420-740 nm range of the VIS light spectrum. The probe light passed various optical elements, the sample, and then a second monochromator, before being detected by a fast photomultiplier tube (Hamamatsu, R9110). Data waves were recorded on a DSA 602A digital signal analyzer (Tektronix, Beaverton, Oregon, USA). Satisfactory signal-to-noise ratios were typically obtained by averaging over 1500 laser shots. The transient absorption measurements were performed on the previously described dye-sensitized, 4 µm-thick, transparent $TiO_2$ either coated with a drop of 3-methylproprionitrile or with the Z960 electrolyte to inhibit degradation. The composition of Z960 is 1.0 M 1,3-dimethylimidazolium iodide, 0.03 M $I_2$, 0.05 M lithium iodide, 0.1 M guanidinium thiocyanate and 0.5 M tert-butylpyridine in acetonitrile and valeronitrile solvent mixture (85:15, v/v).

### 1.5. Photovoltaic device fabrication

Dye sensitized solar cells were fabricated using a double-layered photoanode made of mesoporous $TiO_2$. A transparent, 8-µm-thick layer of 20 nm particles was screen-printed onto a FTO glass pane (NSG-10, Nippon Sheet Glass), pre-treated with $TiCl_4$. Subsequently, a 5-µm-thick layer of scattering particles (300 nm diameter) was screen-printed and the thus formed electrode was sintered up to 500 °C. The $TiCl_4$ post-treatment was performed onto the substrates in order to increase the surface area. The photoanodes were sintered again and after cooling down to 80 °C immersed in a 0.3 mM dye bath with 5mM CDCA in chloroform and ethanol (v/v, 3/7) mixed solution for 3 h at room temperature. The electrode was then rinsed with CH3CN and dried. After rinsing with the same solvent, the stained substrates were sealed with pieces of thermally platinized (a drop of 8 mM hexachloroplatinic solution in 2-propanol, heated to 425 °C) FTO glass (TEC15, Pilkington), which served as a counter electrode. 25-µm-thick Surlyn (Dupont) was used as a binder and a spacer. The electrolytes were introduced to the cells via pre-drilled holes in the counter electrodes. The composition of the electrolyte is as follows: 1.0 M 1,3-dimethylimidazolium iodide, 0.03 M iodine, 0.1 M guanidinium thiocyanate, 0.5 M *tert*-butylpyridine, 0.05 M lithium iodide in acetonitrile:valeronitrile (85:15, v/v).

### 1.6. The electron injection efficiency of the dyes

The electron injection efficiency of **PP-I** and **APP-I** to **IV** dyes at $\lambda_{max}$ was measured as reported earlier and tabulated in Table S1.[S4]

**Table S1.** The electron injection efficiency of **PP-I** and **APP-I** to **IV** dyes

| Dye | IPCE (λ) | Abs (λ) | $\Phi_{inj}$ |
|---|---|---|---|
| **PP-I** | 50.7 | 1.50 | 52.6 |
| **APP-I** | 84.7 | 1.42 | 87.4 |
| **APP-II** | 58.7 | 0.81 | 69.5 |
| **APP-III** | 77.7 | 0.81 | 91.9 |
| **APP-IV** | 78.4 | 1.26 | 82.9 |

### 1.7. Electrochemical studies

#### Transient photovoltage and photocurrent experiment

Both transient decays were measured under varying white light bias provided by a LED array with superimposed red perturbation pulses (also LED). A source meter

(Keithley 2602) was employed to record the voltage dynamics. Photovoltage decays were measured at different open-circuit potentials defined by varying the white light intensity. Cell capacitance was obtained from the integrated photocurrent decay measured close to $V_{oc}$ (varying the light intensity as well). Red perturbation pulses were controlled not to exceed 5 % of the signal resulting from the white bias (either current or voltage) in order to maintain single-exponential decay.[S5]

## Electrochemical impedance spectroscopy (EIS)

The EIS analysis was done on DSC devices at a constant temperature of 20°C in the dark. A sinusoidal potential perturbation with an amplitude of 15 mV was applied over a frequency range 7 MHz – 0.1 Hz (Bio Logic SP300 potentiostat) at constant potential bias. The bias potential varied between 0 mV and Voc with about 50 mV step. The spectra were fitted using ZView software (Scribner Associates) using the transmission model line.[S6] If the potential was corrected for the ohmic losses of the series resistance of the devices it is indicated in the figure caption.

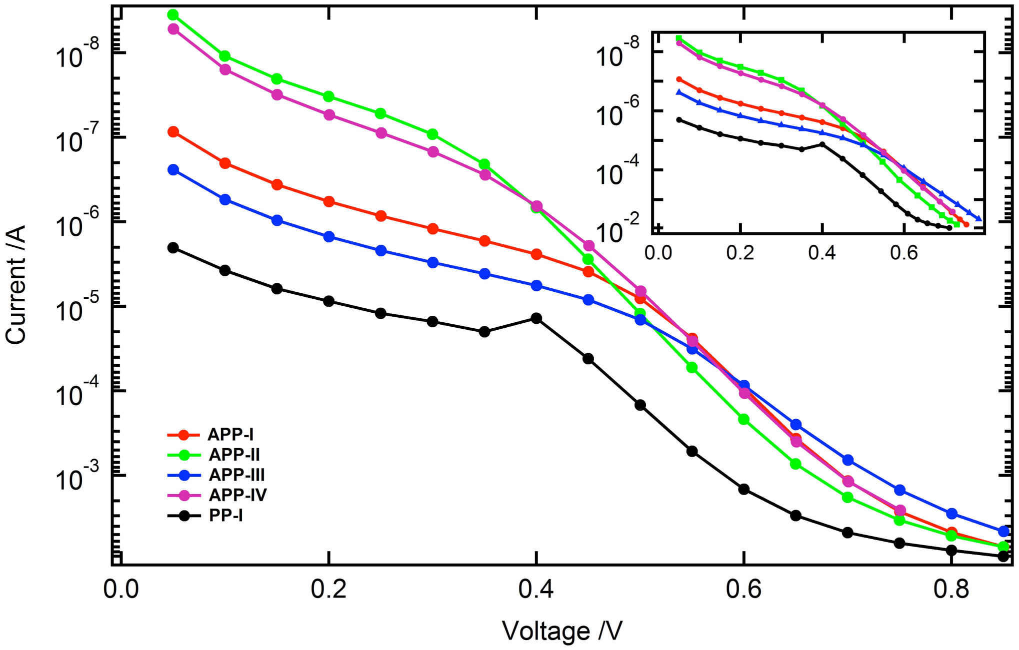


**Figure S3** Dark current characteristic of the investigated devices. Inset shows the plot of the dark current against the IR drop corrected potential

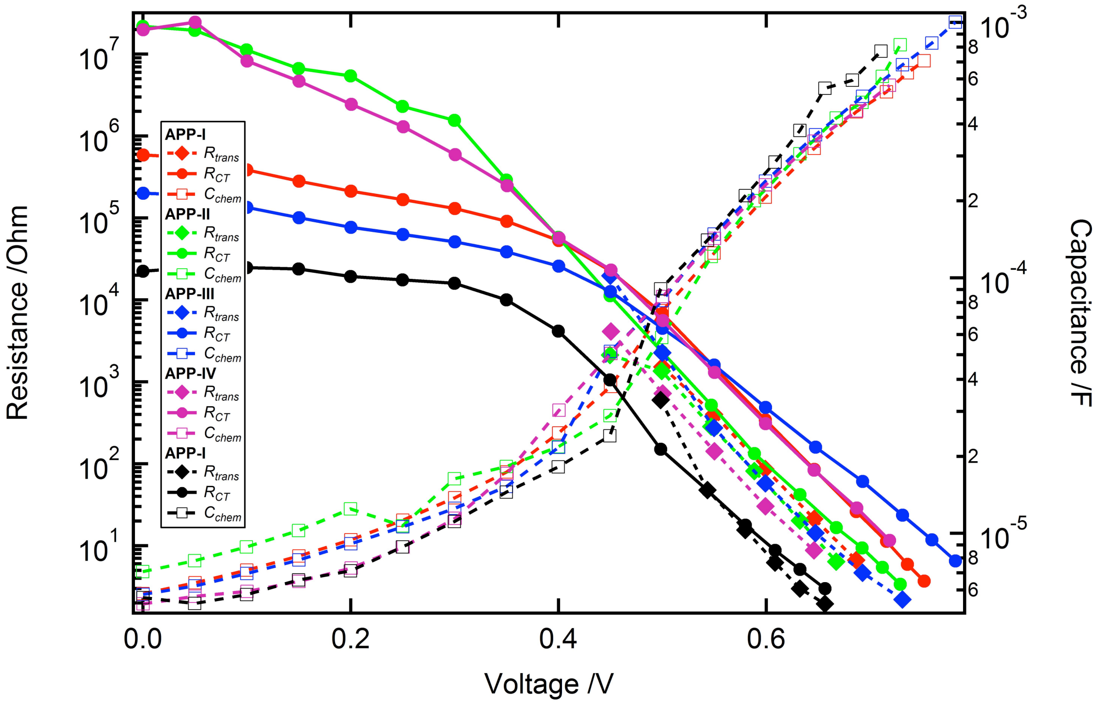


**Figure S4** Transport and recombination resistance as well as the chemical capacitance extracted from the EIS measurements plotted against the IR drop corrected potential.

## 1.8. References

[S1] B.-L. Lee and T. Yamamoto, *Macromolecules*, 1999, **32**, 1375-1382.

[S2] Hua, J.; Mao, J.; Guo, F.; He, N.; Wu, W.; Ying, W.; Tian, H. *CN102532121(A)*, 2012.

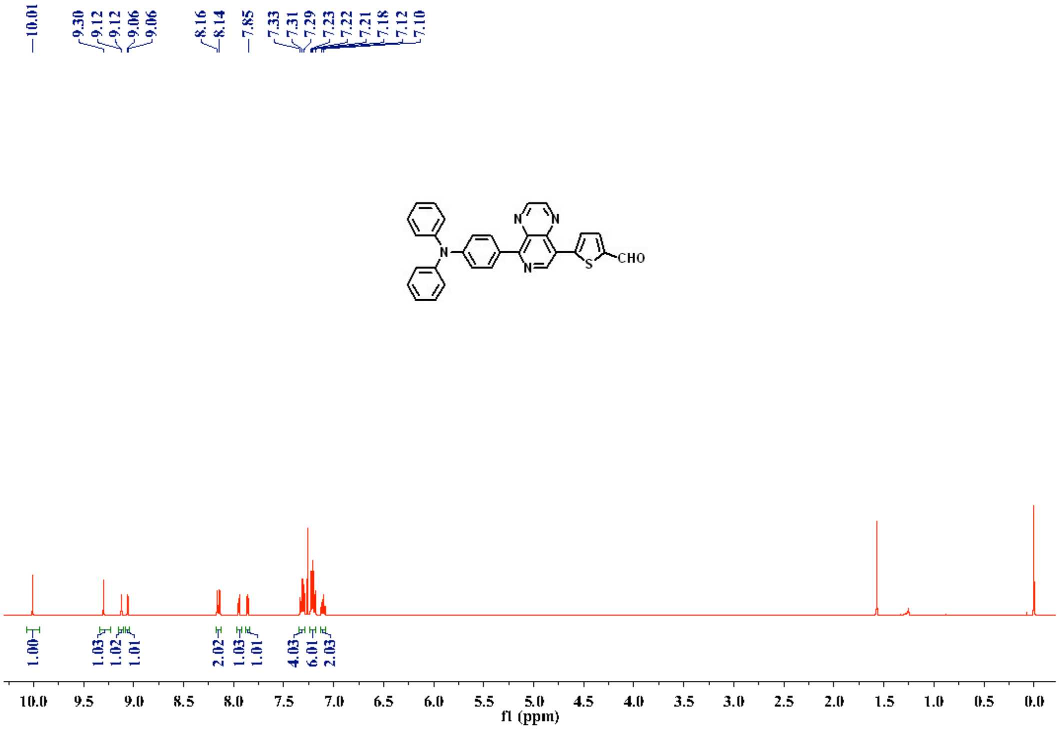
[S3] (a) K. Pei, Y. Z. Wu, Q. Zhang, B. Chen, H. Tian and W. H. Zhu, Chem.-Eur. J., 2012, 18, 8190-8200. (b) Y. Z. Wu and W. H. Zhu, Chem. Soc. Rev., 2013, 42, 2039-2058.

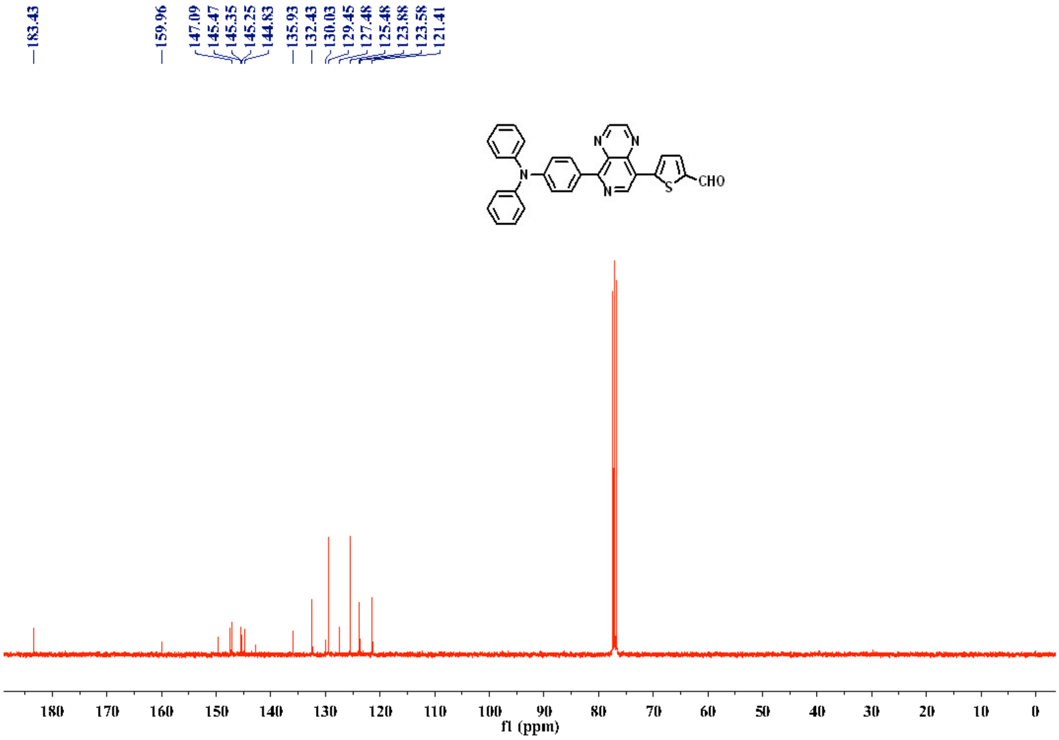
[S4] J. Y. Mao, N. N. He, Z. J. Ning, Q. Zhang, F. L. Guo, L. Chen, W. J. Wu, J. L. Hua and H. Tian, Angew. Chem., Int. Ed., 2012, 51, 9873-9876.

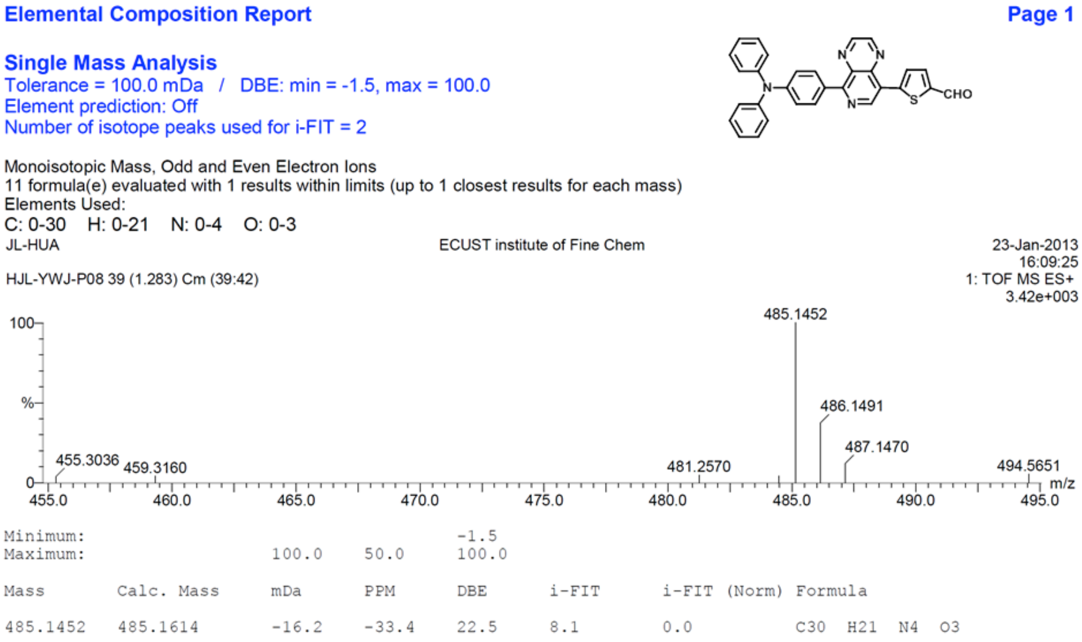
[S5] (a) B. C. O'Regan and F. Lenzmann, J Phys Chem B, 2004, 108, 4342-4350; (b) B. C. O'Regan, K. Bakker, J. Kroeze, H. Smit, P. Sommeling and J. R. Durrant, J Phys Chem B, 2006, 110, 17155-17160.

[S6] (a) F. Fabregat-Santiago, J. Bisquert, G. Garcia-Belmonte, G. Boschloo and A. Hagfeldt, Sol. Energy Mater. Sol. Cells, 2005, 87, 117–131; (b) F. Fabregat-Santiago, G. Garcia-Belmonte, I. Mora-Sero and J. Bisquert, Phys. Chem. Chem. Phys., 2011, 13, 9083–9118.

## 2. ADDITIONAL DATA







**Elemental Composition Report** **Page 1**

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JL-HUA ECUST institute of Fine Chem 23-Jan-2013 16:09:25

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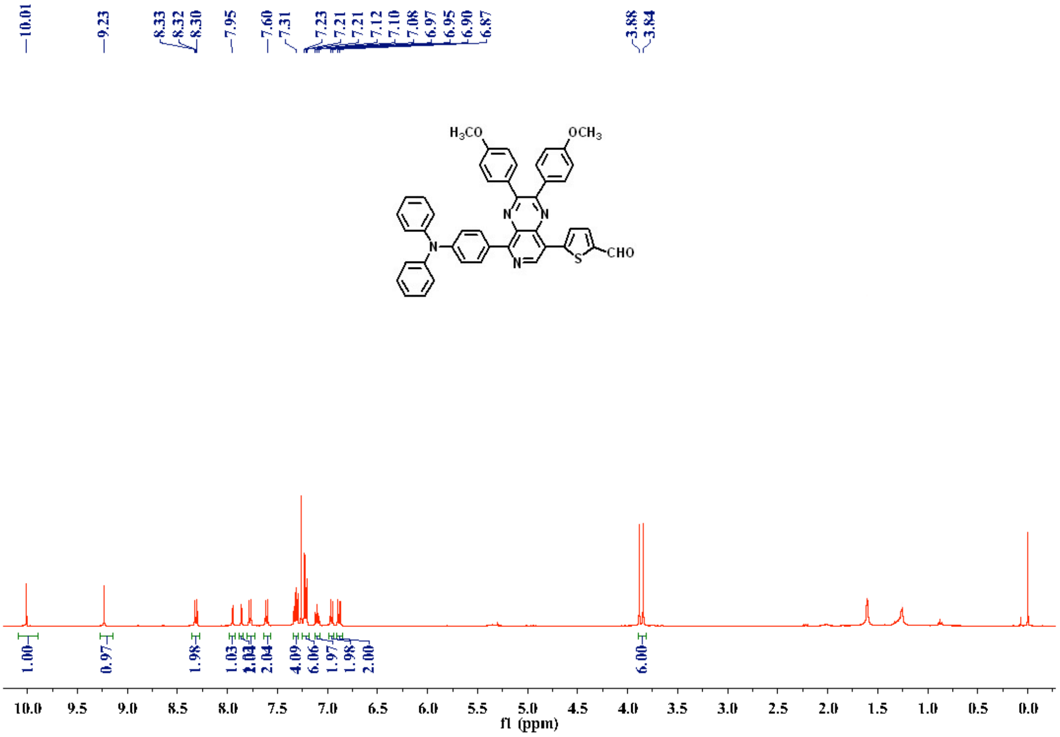

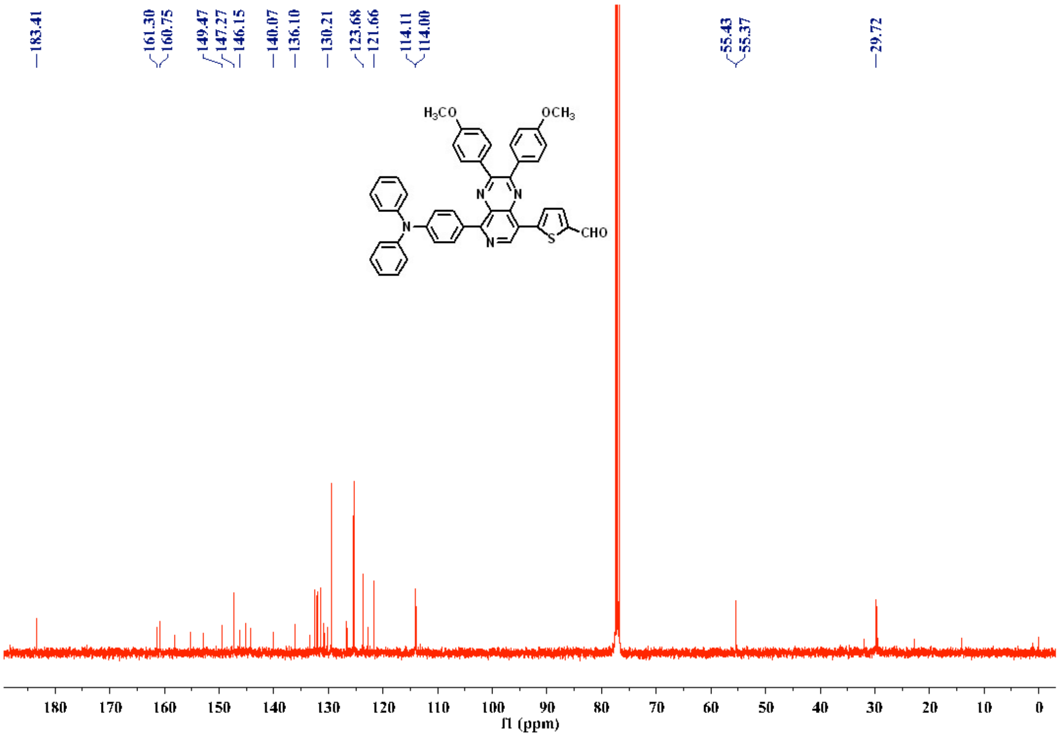

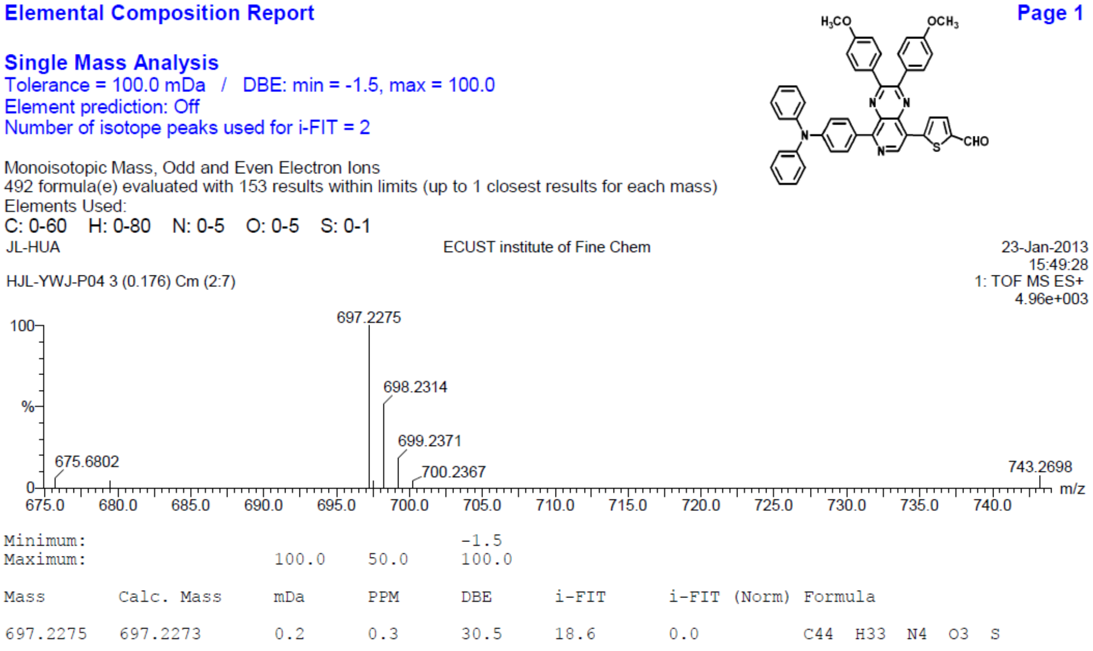

**Elemental Composition Report**

**Page 1**

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JL-HUA
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23-Jan-2013
15:49:28

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4.96e+003

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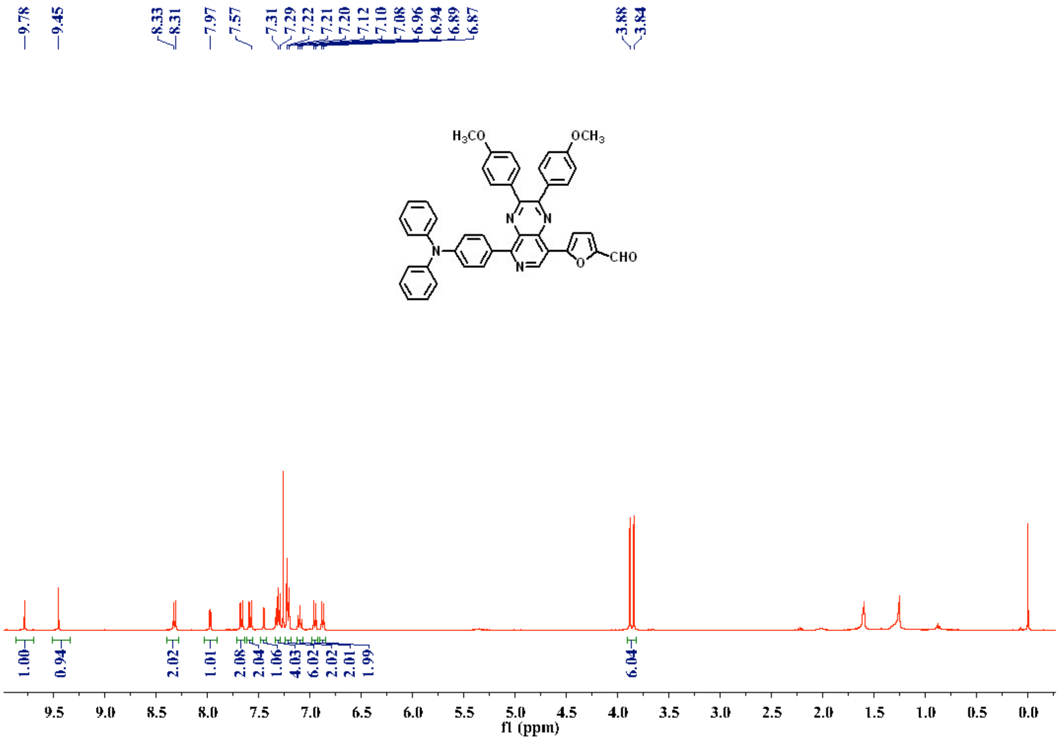
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6.94
6.89
6.87
3.88
3.84
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N
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O
CHO
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2.08
2.04
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4.03
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2.02
2.01
1.99
6.04
9.5
9.0
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8.0
7.5
7.0
6.5
6.0
5.5
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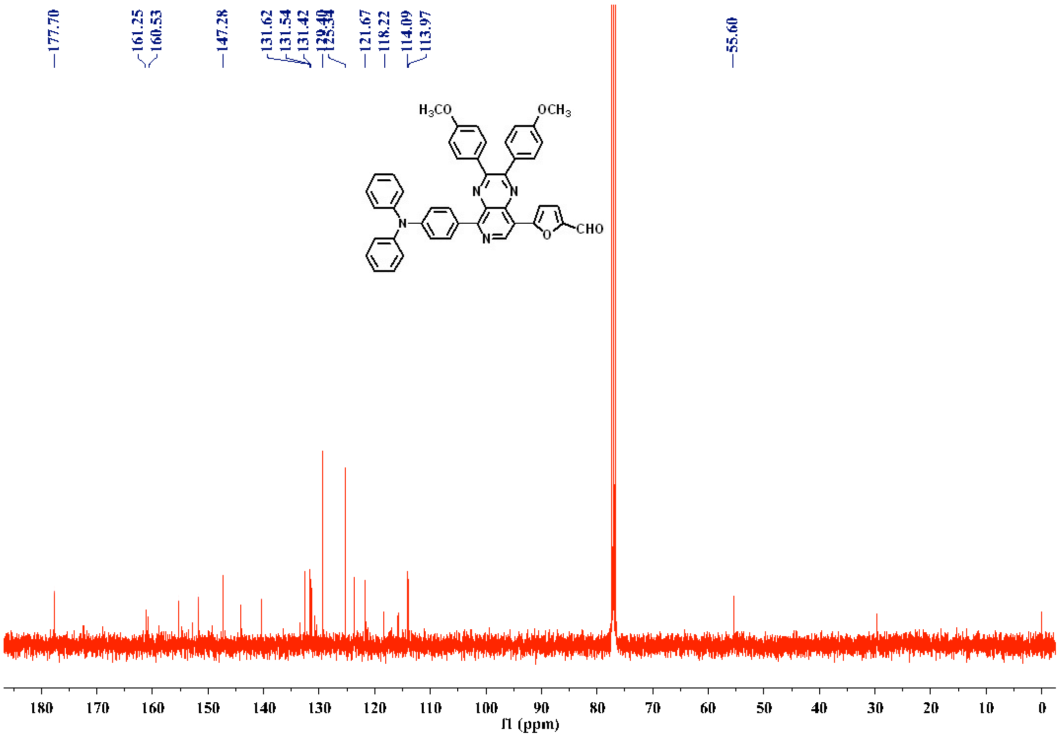
f1 (ppm)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O
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140
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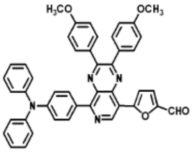
f1 (ppm)

## Elemental Composition Report

Page 1



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Elements Used:
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JL-HUA
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23-Jan-2013
15:31:04

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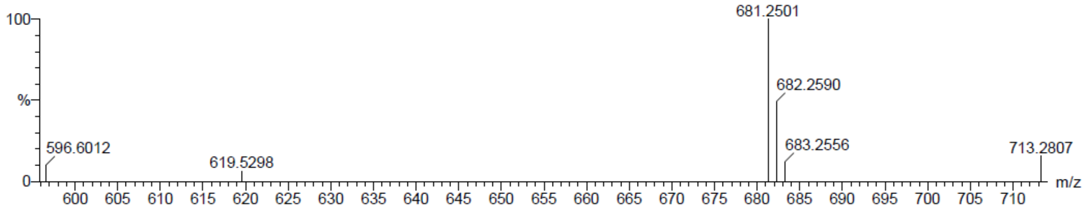

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Maximum:                  100.0     50.0    100.0

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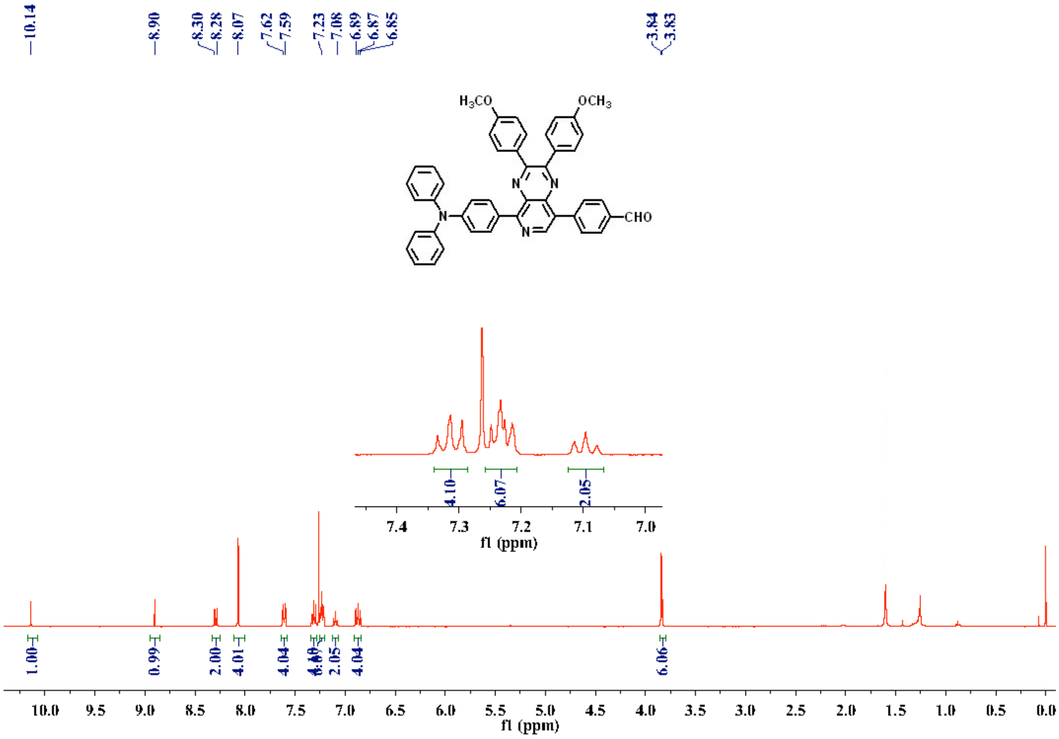

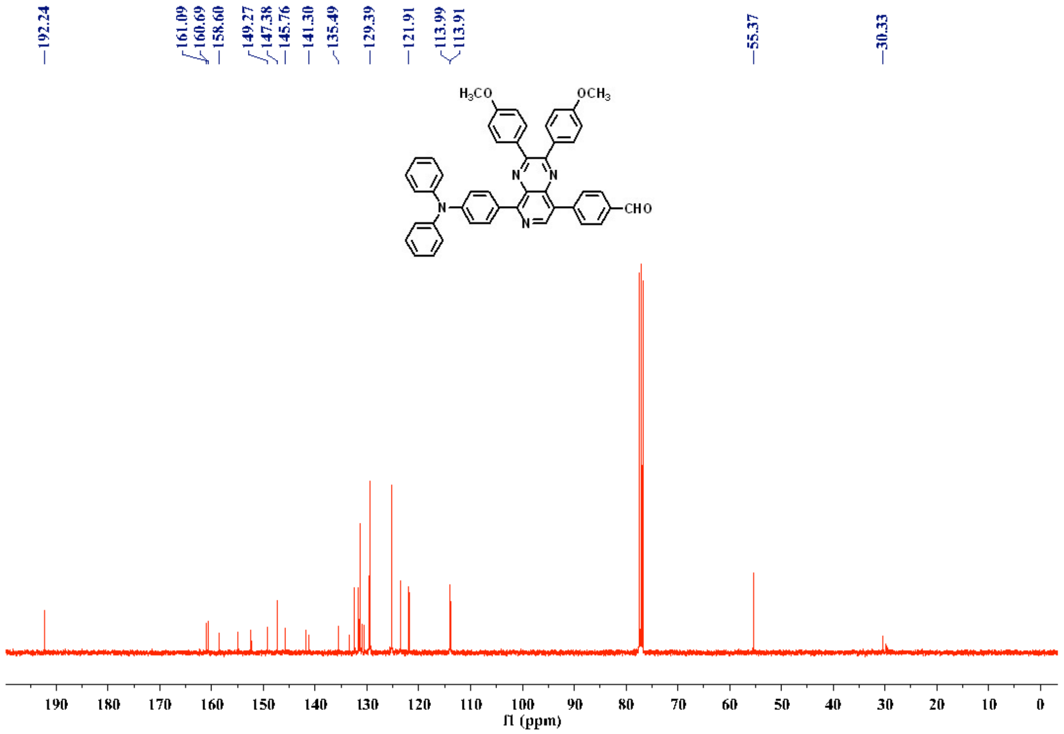

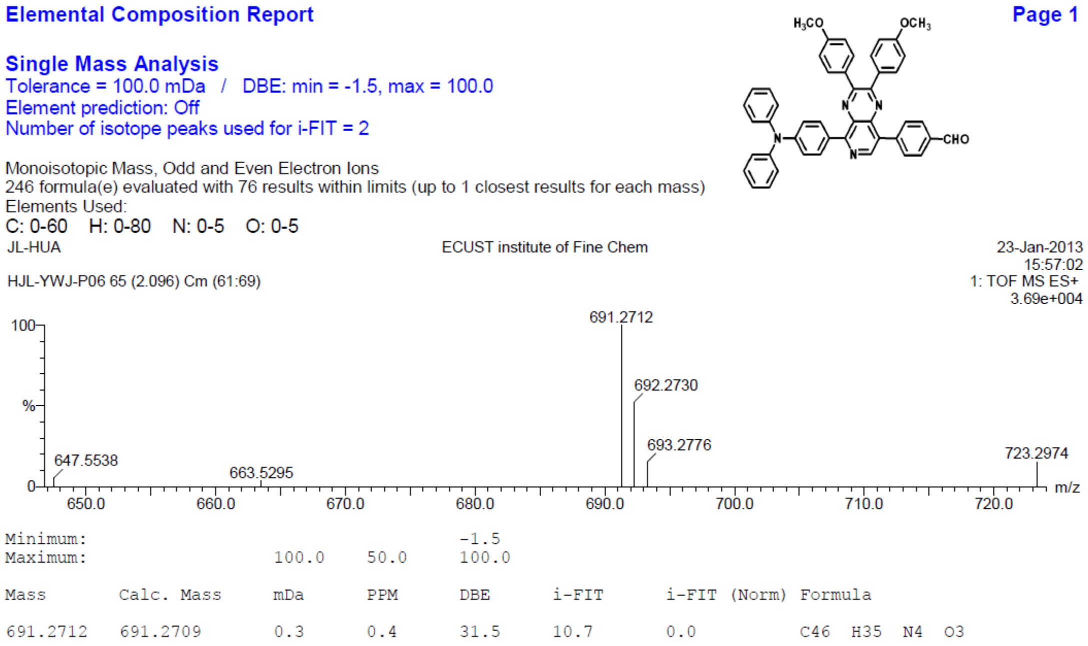

**Elemental Composition Report**

**Page 1**

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Number of isotope peaks used for i-FIT = 2

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JL-HUA
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23-Jan-2013
15:57:02

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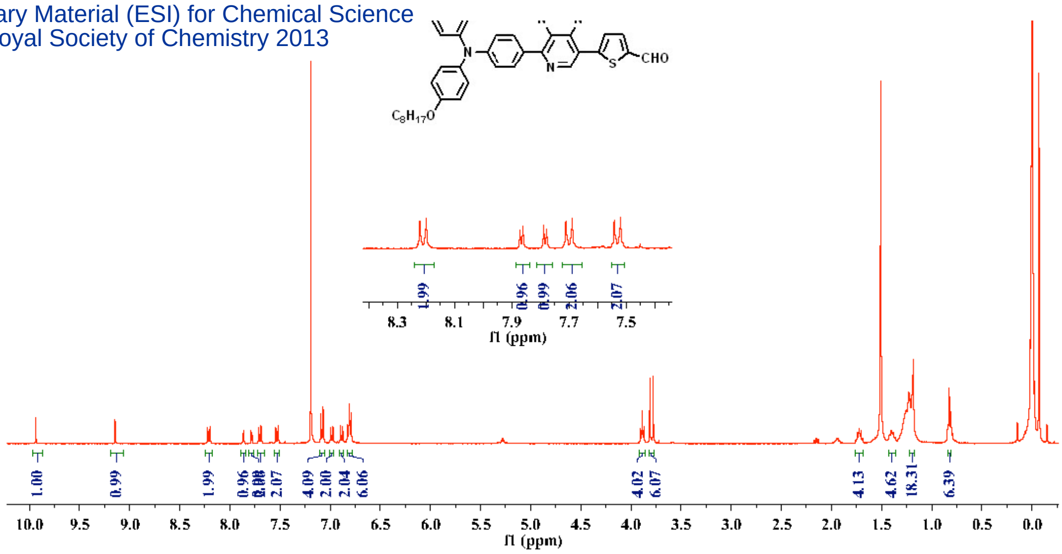
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1.99
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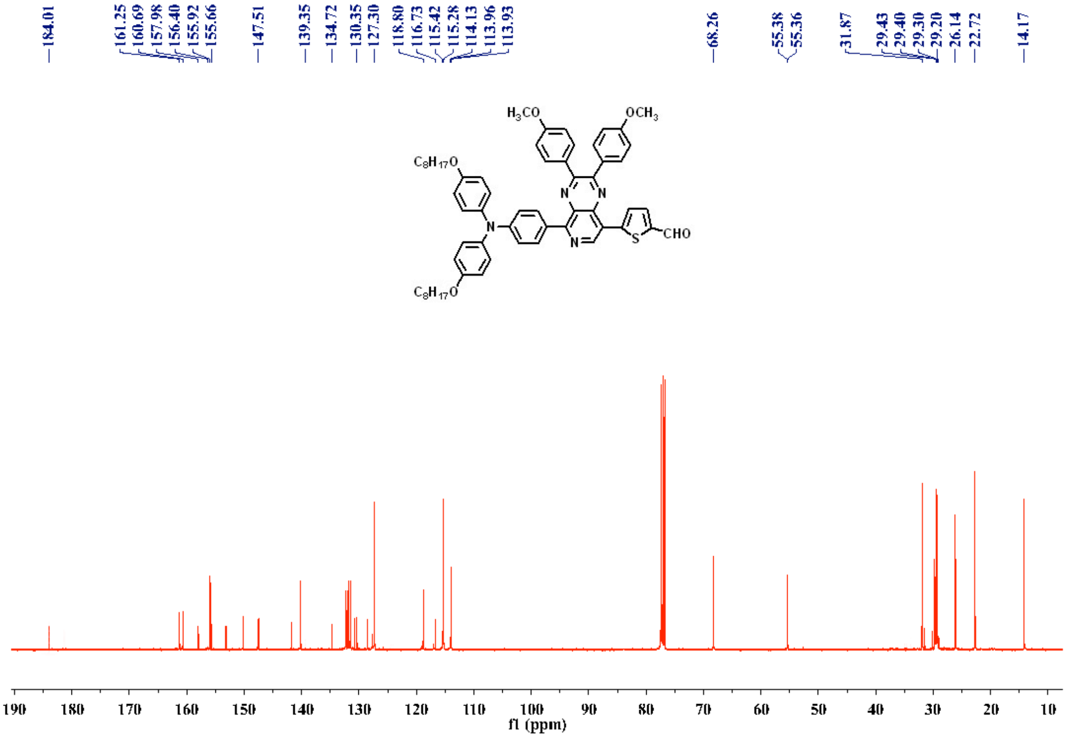
f1 (ppm)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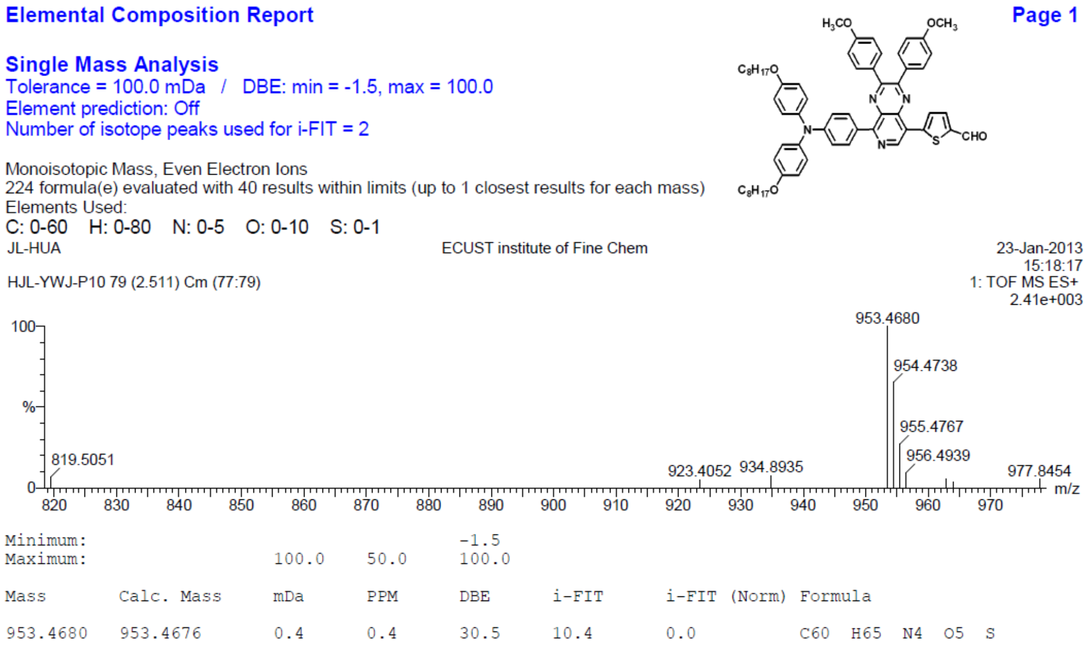

**Elemental Composition Report**

Page 1

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JL-HUA
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23-Jan-2013
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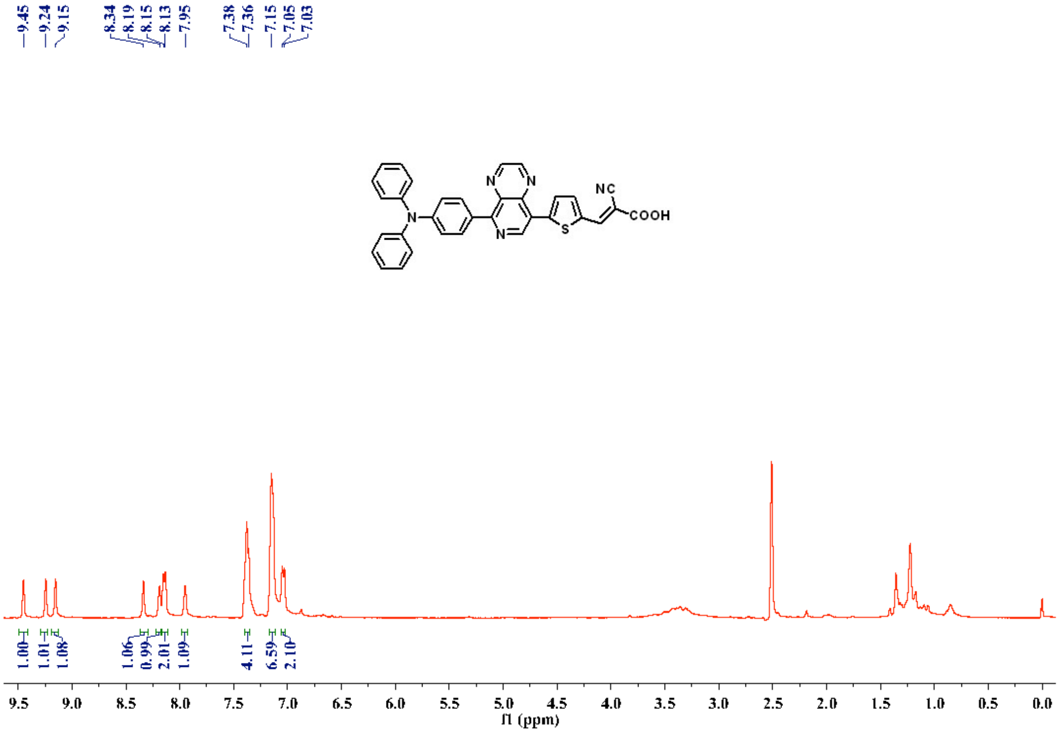

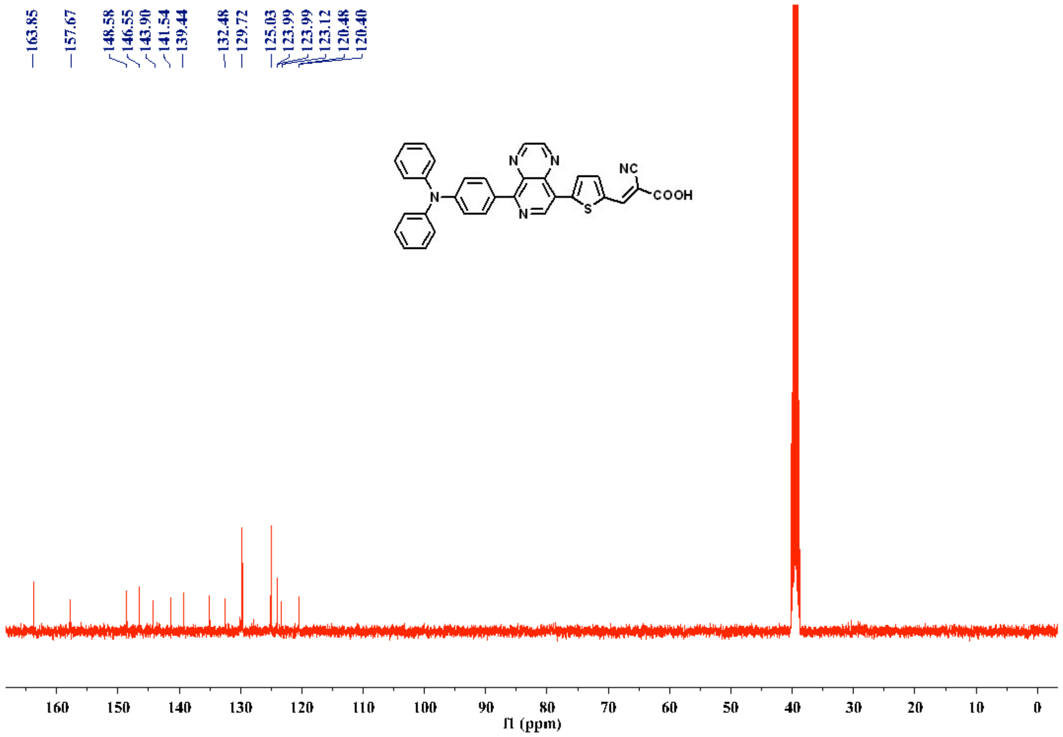

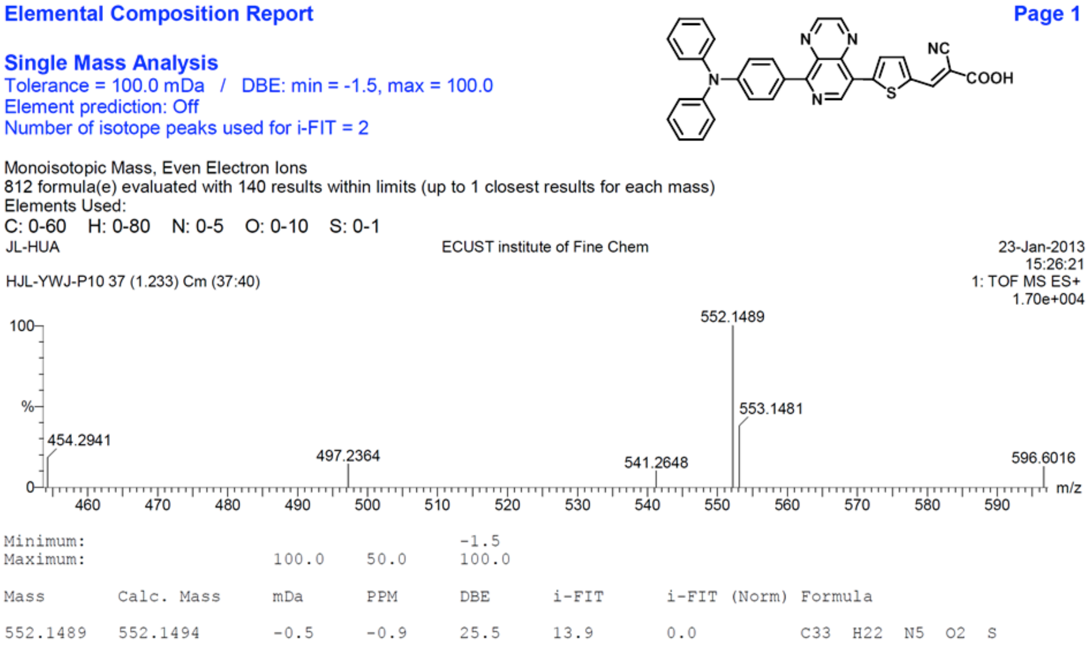

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JL-HUA ECUST institute of Fine Chem 23-Jan-2013
15:26:21

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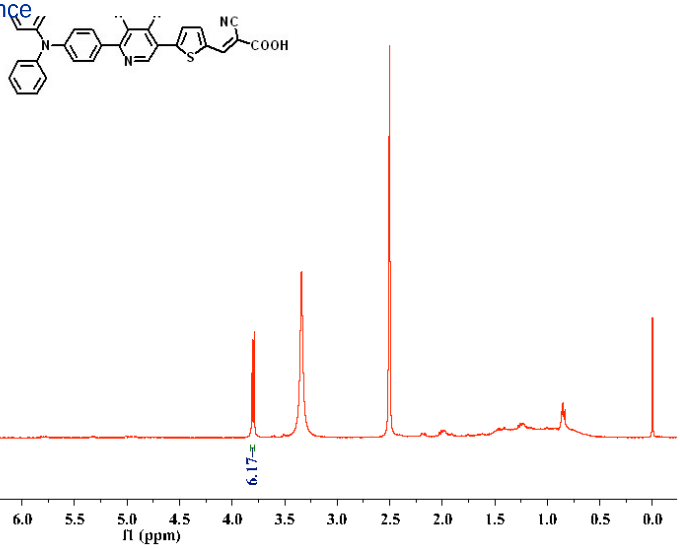
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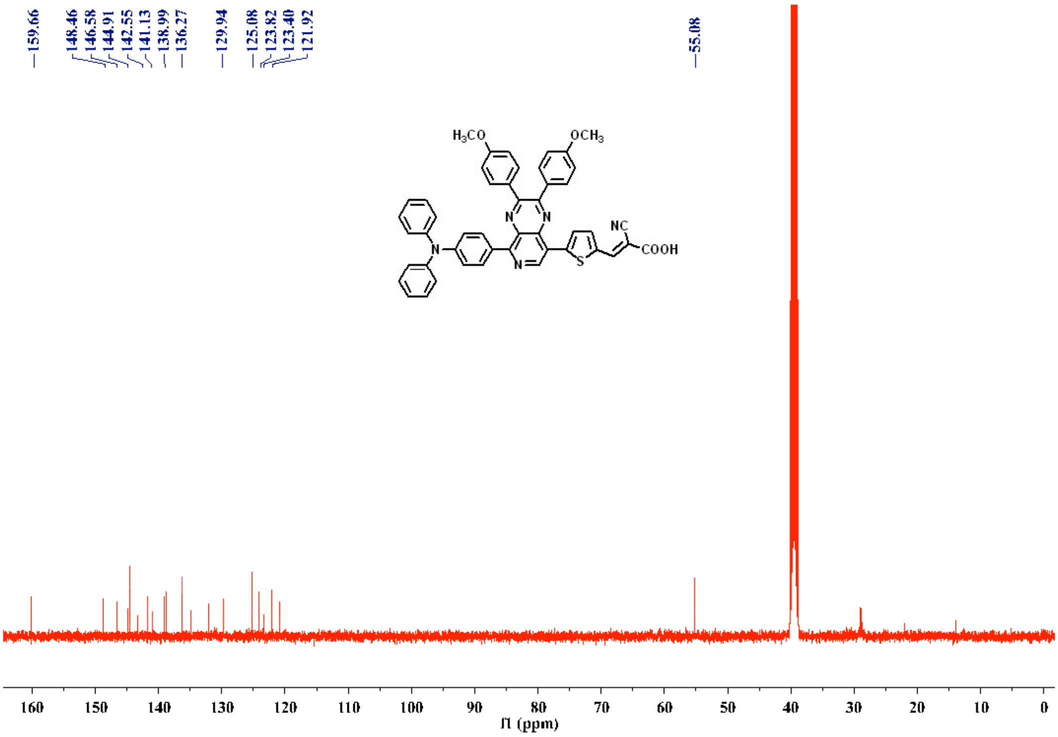
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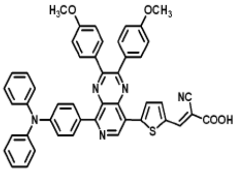
141.13
138.99
136.27
129.94
125.08
123.82
123.40
121.92
55.08
$H_3CO$
$OCH_3$
N
N
N
N
S
NC
COOH
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

**Elemental Composition Report** **Page 1**

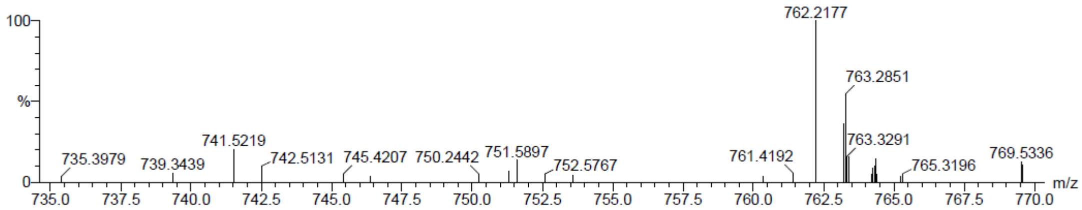


**Single Mass Analysis**
Tolerance = 50.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

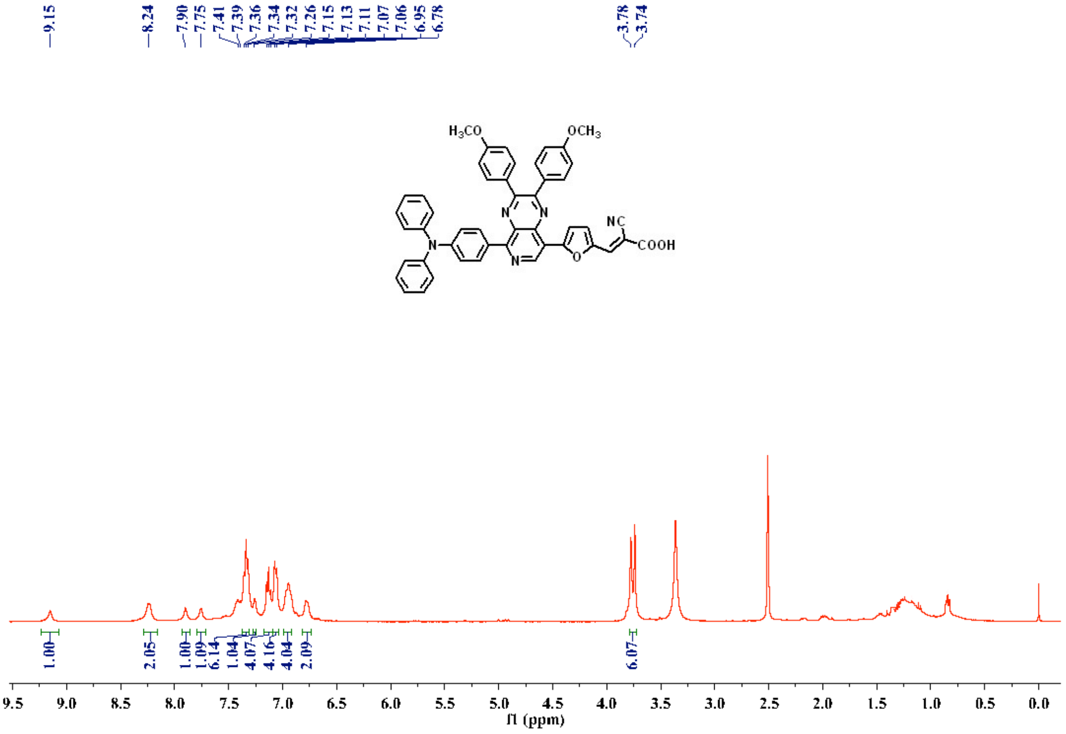
Monoisotopic Mass, Even Electron Ions
1218 formula(e) evaluated with 63 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-63 H: 0-120 N: 0-6 O: 0-9 S: 0-1

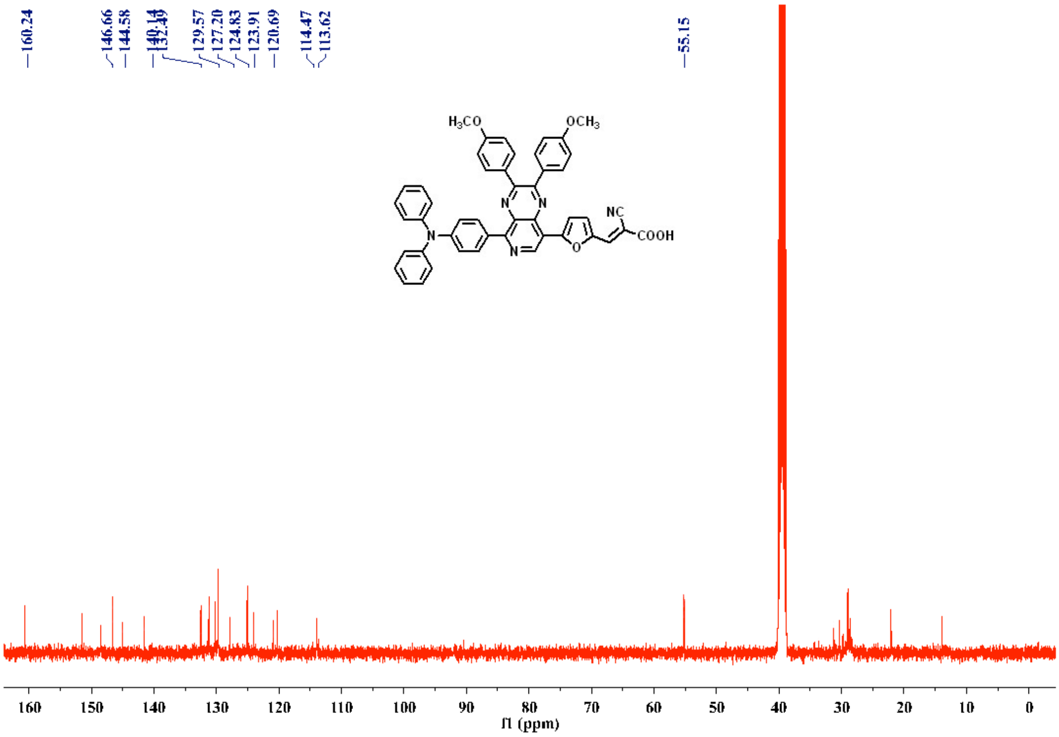
JL-HUAN ECUST institute of Fine Chem 07-Oct-2012
14:26:10

HJL-YWJ-TP1 19 (0.687) Cm (17:20) 2: TOF MS ES-
1.35e+003

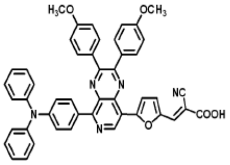


```
Minimum:                                  -1.5
Maximum:                 50.0     50.0    100.0

Mass      Calc. Mass     mDa      PPM     DBE       i-FIT     i-FIT (Norm) Formula

762.2177  762.2175       0.2      0.3     34.5      50.7      0.0          C47  H32  N5  O4  S
```





**Elemental Composition Report** **Page 1**

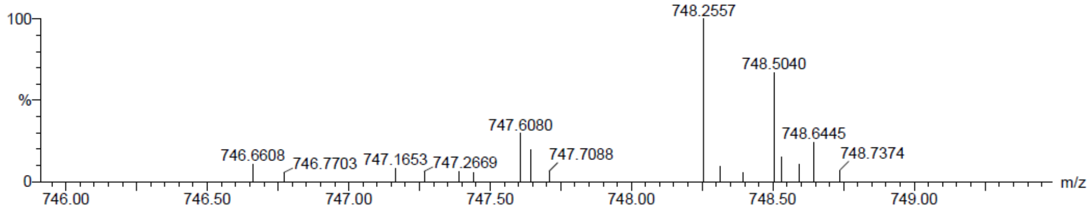


**Single Mass Analysis**
Tolerance = 50.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

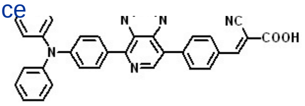
Monoisotopic Mass, Even Electron Ions
389 formula(e) evaluated with 17 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-50 H: 0-120 N: 0-6 O: 0-9

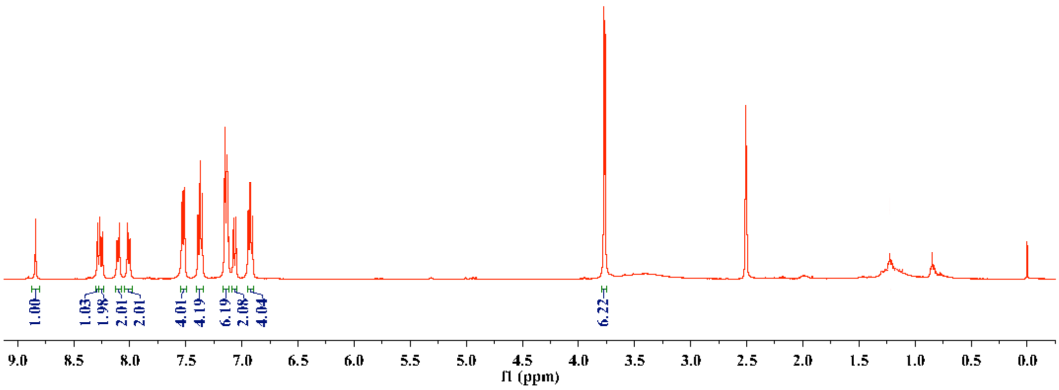
JL-HUAN
ECUST institute of Fine Chem
07-Oct-2012
14:16:56

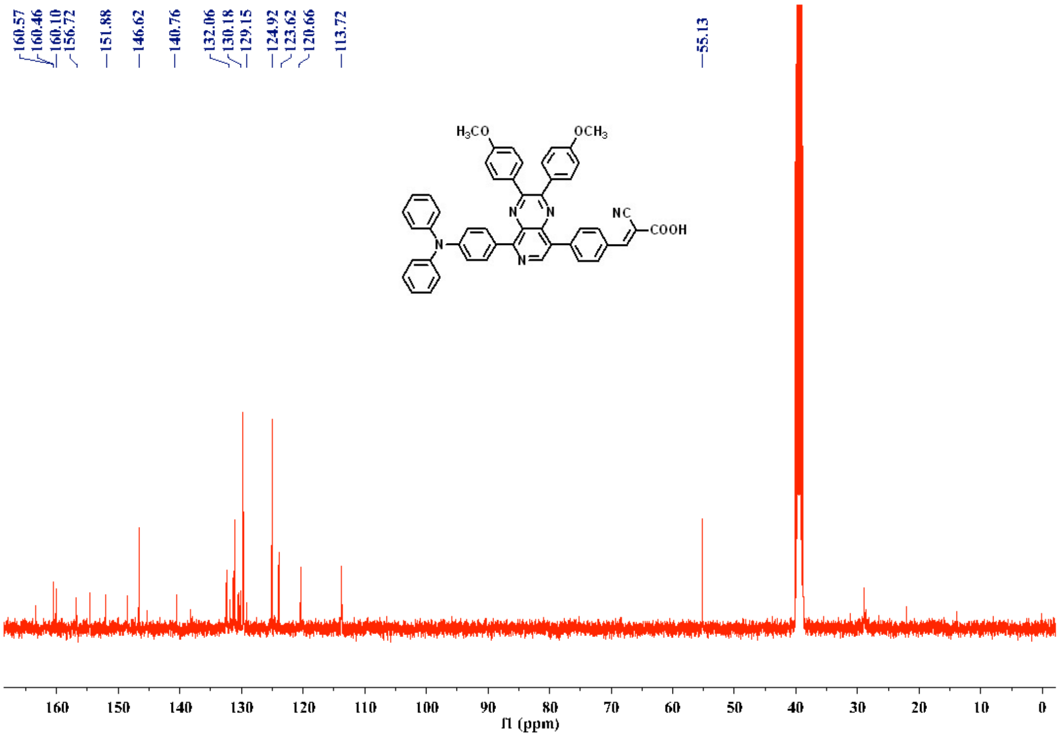
HJL-YWJ-TP2 80 (2.542) Cm (78:83)
1: TOF MS ES+
1.48e+002



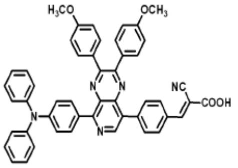
```
Minimum:                                 -1.5
Maximum:              50.0      50.0     100.0

Mass      Calc. Mass  mDa       PPM      DBE       i-FIT      i-FIT (Norm)  Formula

748.2557  748.2560    -0.3      -0.4     33.5      60.2       0.0           C47  H34  N5  O5
```


N
N
N
N
NC
COOH


1.00
1.03
1.98
2.01
2.01
4.01
4.19
6.19
2.08
4.04
6.22
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


160.57
160.46
160.10
156.72
151.88
146.62
140.76
132.06
130.18
129.15
124.92
123.62
120.66
113.72
55.13
H3CO
OCH3
N
N
N
N
NC
COOH
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

## Elemental Composition Report



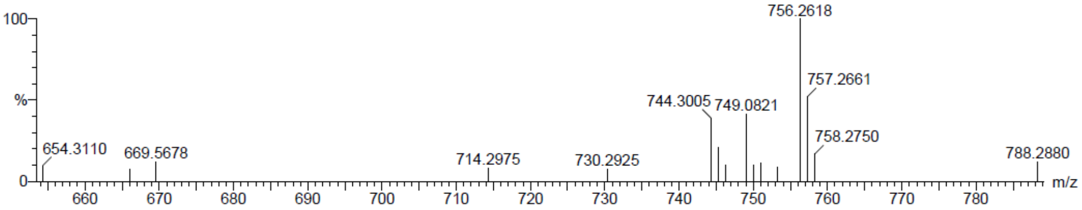
### Single Mass Analysis

Tolerance = 100.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

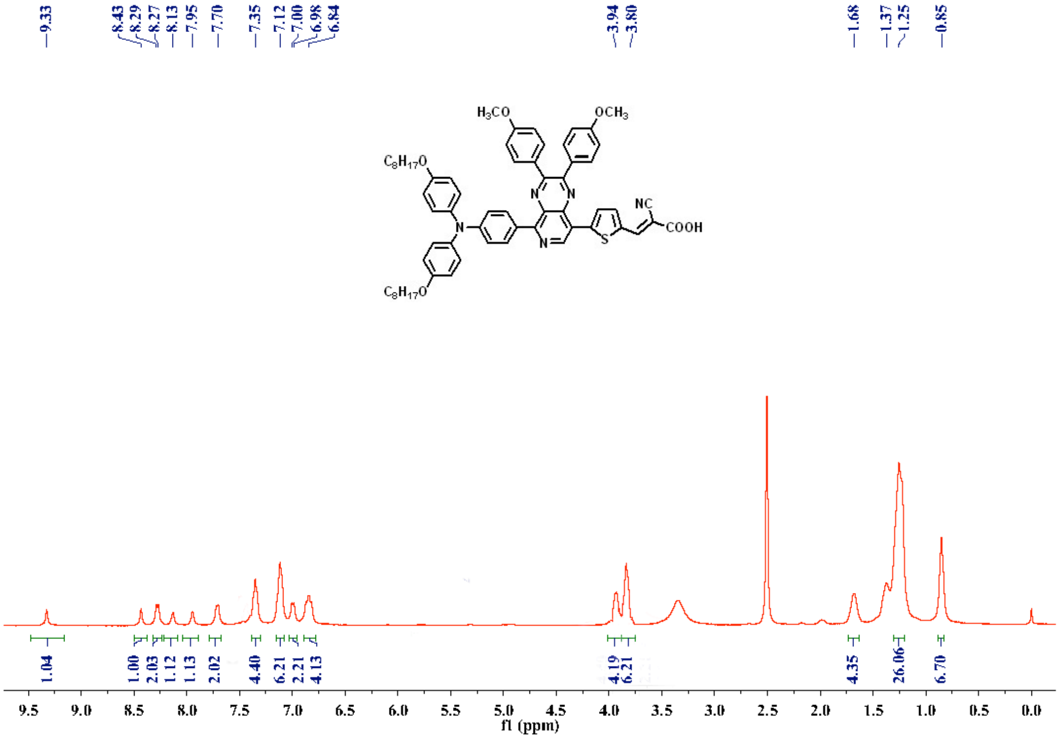
Monoisotopic Mass, Even Electron Ions
14 formula(e) evaluated with 2 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-49 H: 0-50 N: 0-5 O: 0-4

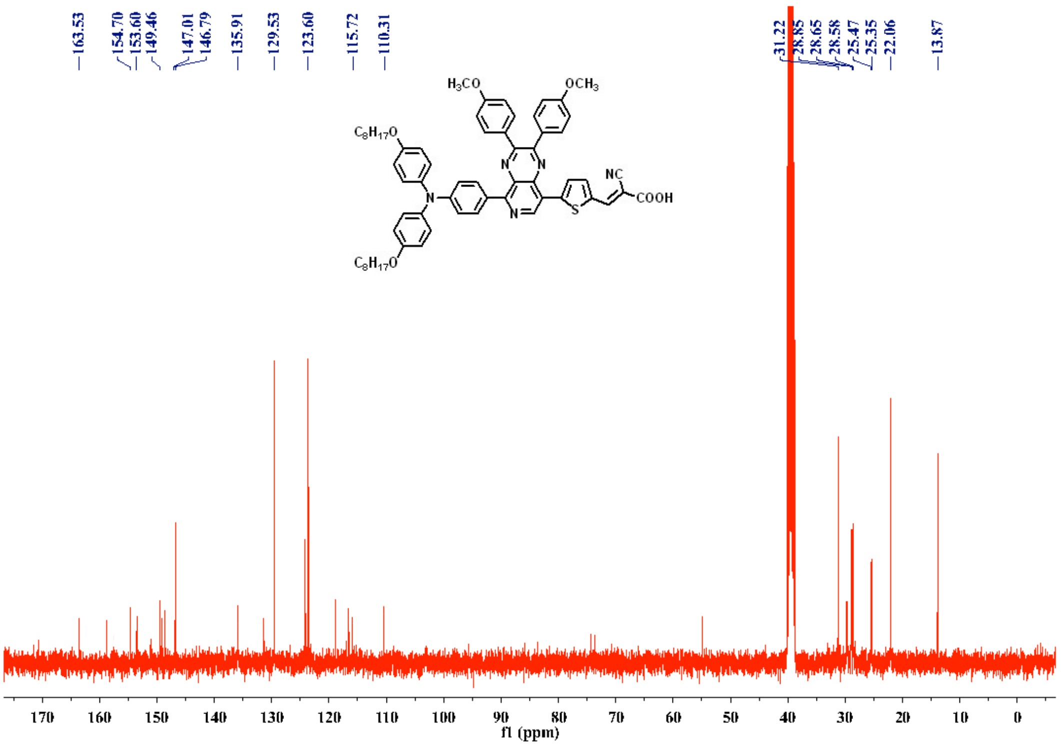
JL-HUAN ECUST institute of Fine Chem 04-Jan-2013 20:04:34

HJL-YWJ-TPP3 34 (1.156) Cm (33:34) 2: TOF MS ES- 1.27e+003



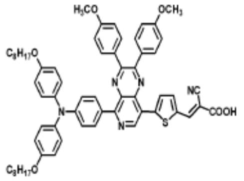
```
Minimum:                                      -1.5
Maximum:                  100.0     50.0      100.0

Mass      Calc. Mass      mDa       PPM       DBE       i-FIT      i-FIT (Norm) Formula

756.2618  756.2611        0.7       0.9       35.5      8.8        0.0          C49  H34  N5  O4
```





## Elemental Composition Report

Page 1



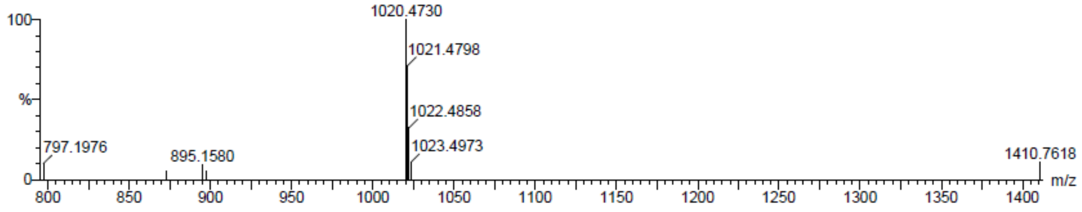
### Single Mass Analysis

Tolerance = 100.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Odd and Even Electron Ions
443 formula(e) evaluated with 172 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-70 H: 0-80 N: 0-5 O: 0-10 S: 0-1

JL-HUA ECUST institute of Fine Chem 23-Jan-2013
14:58:30

HJL-YWJ-P12 18 (0.644) Cm (12:18) 1: TOF MS ES+
1.76e+004



```
Minimum:                                      -1.5
Maximum:                   100.0      50.0    100.0

Mass       Calc. Mass      mDa        PPM     DBE        i-FIT       i-FIT (Norm) Formula

1020.4730  1020.4734       -0.4       -0.4    33.5       13.9        0.0          C63  H66  N5  O6  S
```