

Electronic Supplementary Information

Quinoxaline Based *N*-Heteroacene Interfacial Layer for Efficient Hole-Injection in Quantum Dot Light-Emitting Diodes

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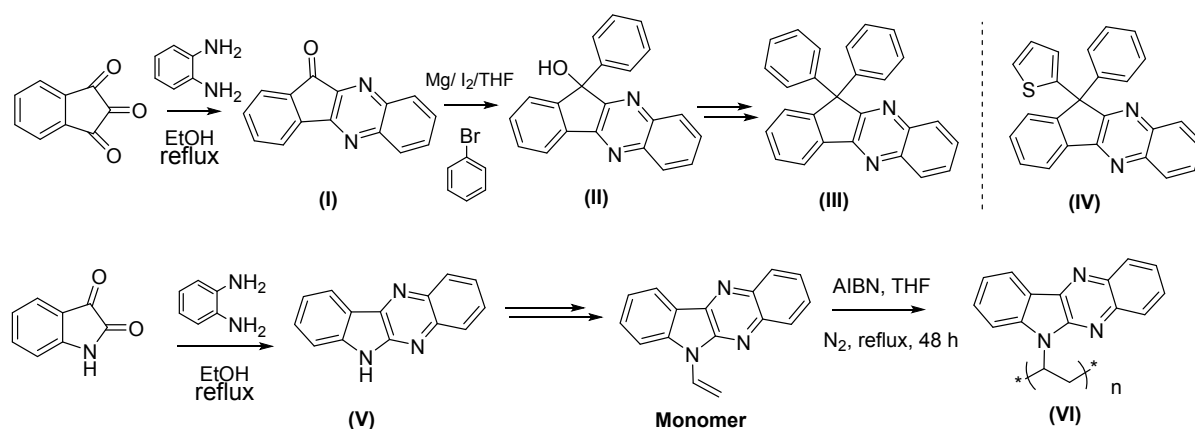
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1. General information

General. All reagents and solvents were purchased from Sigma Aldrich and used as per received without further purification. ^1H NMR and ^{13}C NMR spectra were measured on BBFO-400 spectrometer. High resolution mass spectrometry (HRMS) was performed on a Waters Q-tof Premier MS spectrometer. Absorption spectra were recorded on a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer, while the fluorescent emission spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. Fourier transform infrared (FT-IR) spectra were collected with an SHIMADZU IR Prestige-21 spectrometer. Thermal-gravimetric analyses (TGA) were performed on a TGA 500 thermo gravimetric analyzer by heating the samples at $10\text{ }^\circ\text{C min}^{-1}$ to $500\text{ }^\circ\text{C}$ in a nitrogen atmosphere.

2. Materials synthesis and characterization



Scheme 1. Synthesis of N-heteroacene quinoxaline derivatives.

2.1 Compound (I): A mixture of 1H-indene-1,2,3-trione (2.00 g, 13.23 mmol) and benzene-1,2-diamine (1.34 g, 12.35 mmol) in ethanol (56 mL) was heated to reflux under stirring for 4h. After cooling to room temperature, the reaction mixture was filtered and washed by ethanol. 11H-indeno[1,2-b]quinoxalin-11-one (**I**) as yellow powder was then obtained (yield 96%). GC-MS (EI-m/z): 232 (M^+). ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 1.4$ Hz, 1H), 8.11 – 8.06 (m, 2H), 7.91 (d, $J = 7.5$ Hz, 1H), 7.82 – 7.71 (m, 3H), 7.59 (td, $J = 7.5, 1.0$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 189.89 (s), 156.61 (s), 149.27 (s), 143.12 (s), 142.64 (s), 141.54 (s), 136.80 (s), 136.67 (s), 132.50 (s), 132.44 (s), 131.60 (s), 130.28 (s), 129.67 (s), 124.77 (s), 122.51 (s).

2.2 Compound (II): A mixture of Mg (0.21g, 8.62mmol) and a small amount of iodine in THF (2 mL) was put into a round bottom flask with three necks under N_2 atmosphere. Then, a 50 mL constant pressure drop funnel containing bromobenzene (0.9 mL) and THF (30 mL), was equipped onto the flask. A heat gun was used to activate this reaction. The color of the solution became colorless, indicating that this reaction was activated successfully. After the activation, the flask was located in an ice bath, and the bromobenzene solution was started to drop under stirring. After the dropping, this reaction flask was transferred into an oil bath and heated at $40\text{ }^\circ\text{C}$ for 3 h. A solution of compound (**I**) (1.00g, 4.31 mmol) in THF was dropped into the solution slowly. The mixture was heated to reflux with stirring for overnight. This reaction was quenched by a saturated solution of NH_4Cl . The crude product was purified by flash chromatography to obtain yellow powder compound II (yield 37%). GC-MS (EI-m/z): 310(M^+). ^1H NMR (400 MHz, CDCl_3) δ 8.14 – 8.05 (m, 2H), 7.99 (dd, $J = 8.2, 1.2$ Hz, 1H), 7.74 – 7.69 (m, 1H), 7.67 – 7.62 (m, 1H), 7.53 – 7.44 (m, 3H), 7.44 – 7.39 (m, 2H), 7.33 – 7.22

(m, 4H), 3.77 (s, 1H). ¹³C NMR (400 MHz, CDCl₃, ppm): δ 141.54, 136.82, 132.47, 131.61, 130.29, 130.11, 130.04, 129.67, 129.15, 128.48, 127.89, 125.81, 125.53, 124.79, 122.55, 122.30, 53.43.

2.3 Compound (III): compound (II) (0.58g, 2.50 mmol) in benzene (3 mL) was prepared first. Trifluoroacetic acid (7.0 mL) was dropped into the above solution slowly, and the mixture was heated at 50 °C for 12h. Then, the reaction mixture was transferred to an ice bath and NaOH was used to change the pH of the solution from acidic to basic. After the reaction, DCM was used to extract the product and Na₂SO₄ was used as drier. The crude product was purified by flash chromatography to obtain yellow powder compound (III) (yield 33%). GC-MS (EI-m/z): 370(M⁺). ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.29-8.28 (t, *J*=7.2, 1H), 8.16-8.14 (d, *J*=8.4, 1H), 8.10-8.08 (d, *J*=8.4, 1H), 7.75-7.71 (t, *J*=6.8, 1H), 7.69-7.65 (t, *J*=14.8, 1H), 7.56-7.54 (d, *J*=8.4, 2H), 7.54-7.53 (t, *J*=6.8, 1H), 7.31-7.29 (m, 5H), 7.26-7.24 (m, 5H). ¹³C NMR (400 MHz, CDCl₃, ppm): δ 165.14, 154.23, 151.41, 143.70, 142.28, 141.90, 136.48, 131.75, 129.83, 129.62, 129.00, 128.81, 128.71, 128.65, 128.62, 128.30, 127.34, 127.15, 122.79, 62.73.

2.4 Compound (IV): Compound (II) (0.30g, 0.97mmol) in DCM (25 mL) was prepared first. The BF₃•Et₂O solution (0.15 mL) was dropped into the above solution slowly, and the mixture was stirred under room temperature for a while. Then, thiophene (0.076 mL, 0.97mmol) in DCM was added. After 12 h, this reaction was quenched by water. The crude product was purified by flash chromatography to obtain yellow powder compound IV (yield 53%). GC-MS (EI-m/z): 376(M⁺). ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.28-8.26 (d, *J*=8, 1H), 8.17-8.15 (d, *J*=8, 1H), 8.14-8.12 (d, *J*=8.4, 1H), 7.77-7.75 (d, *J*=7.6, 1H), 7.73-7.71 (d, *J*=7.6, 1H), 7.67-7.55 (t, *J*=10, 2H), 7.58-7.56 (t, *J*=8, 2H), 7.25-7.22 (m, 5H), 7.07-7.06 (d, *J*=3.2, 1H), 6.93-6.90 (t, *J*=12.8, 1H). ¹³C NMR (400 MHz, CDCl₃, ppm): δ 164.42, 153.68, 151.46, 146.08, 143.32, 142.45, 141.79, 136.25, 131.79, 129.81, 129.08, 128.97, 128.36, 128.06, 127.64, 127.46, 126.95, 126.40, 125.61, 122.68, 59.51.

2.5 Compound (V): A mixture of indoline-2,3-dione (2.00 g, 13.60 mmol) and benzene-1,2-diamine (1.64 g, 14.80 mmol) in ethanol (80 mL) was heated to reflux with stirring for overnight. After cooling to room temperature, the reaction mixture was filtered and washed by ethanol. 6H-indolo[2,3-b]quinoxaline (V) as yellow powder was obtained (yield 89%). HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₄H₉N₃, 220.0875; found, 220.0877. ¹H NMR (400 MHz, DMSO) δ 12.04 (s, 1H), 8.37 – 8.33 (m, 1H), 8.26 (dd, *J* = 8.3, 1.1 Hz, 1H), 8.07 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.81 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.75 – 7.68 (m, 2H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.40 – 7.34 (m, 1H). ¹³C NMR (101 MHz, DMSO) δ 146.33 (s), 144.48 (s), 140.62 (s), 140.27 (s), 139.07 (s), 131.77 (s), 129.51 (s), 129.19 (s), 127.95 (s), 126.41 (s), 122.70 (s), 121.16 (s), 119.45 (s), 112.46 (s).

2.6 Monomer: A mixture of 1,2-dichloroethane (16ml, 195.70 mmol), KOH (2.2g, 39.40 mmol), K₂CO₃ (1.8g, 12.80 mmol), tetrabutylammoniumbromide (0.04 g, 0.13 mmol), the compound (V) (1.2g, 5.60 mmol) were heated to 60°C for overnight. After cooling to room temperature, the mixture was extracted by CH₂Cl₂. The solvent was removed by rotary evaporation. The crude product was used to prepare another mixture of crude powder (1.5g, 5.30 mmol), KOH (1.2g, 21.40 mmol), hydroquinone (0.03 g, 0.27 mmol), 35ml isopropanol were heated to reflux for 4h. After cooling to room temperature, the mixture was extracted by CH₂Cl₂. The solvent was removed by rotary evaporation. The crude product was purified by silica gel chromatography using hexane/ ethyl acetate=3:1 as an eluent to isolate pure monomer (Yield 93%). HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₆H₁₁N₃, 246.1031; found, 246.1034. ¹H NMR (400 MHz, DMSO) δ 8.39 (d, *J* = 7.4 Hz, 1H), 8.27 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.85 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.80 (tdd, *J* = 4.7, 3.6, 1.2 Hz, 2H), 7.70 (dd, *J* = 15.9, 9.6 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 6.49 (d, *J* = 15.9 Hz, 1H), 5.26 (d, *J* = 9.6

Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 132.28 (s), 129.85 (s), 129.49 (s), 128.45 (s), 128.18 (s), 127.63 (s), 123.01 (s), 122.69 (s), 111.76 (s), 102.90 (s).

2.7 Polymer (VI, or PVI): A mixture of monomer (0.50g, 2.0 mmol) and AIBN (0.001g, 0.0061 mmol) in THF (2 mL) was put into a Schlenk tube. The tube was cooled down in liquid N_2 and was evacuated to remove O_2 inside for 3 times. Then, the mixture was heated to reflux for 48h. During this period, the solid materials were gradually dissolved. At the end of the reaction, hexane was added to induce the precipitation. The obtained precipitates were extracted by acetone for 48h. The solid materials were collected and examined by MALDI-TOF. $M_n = 3500$, $M_w = 4700$, $pd = 1.33004$.

3. TGA

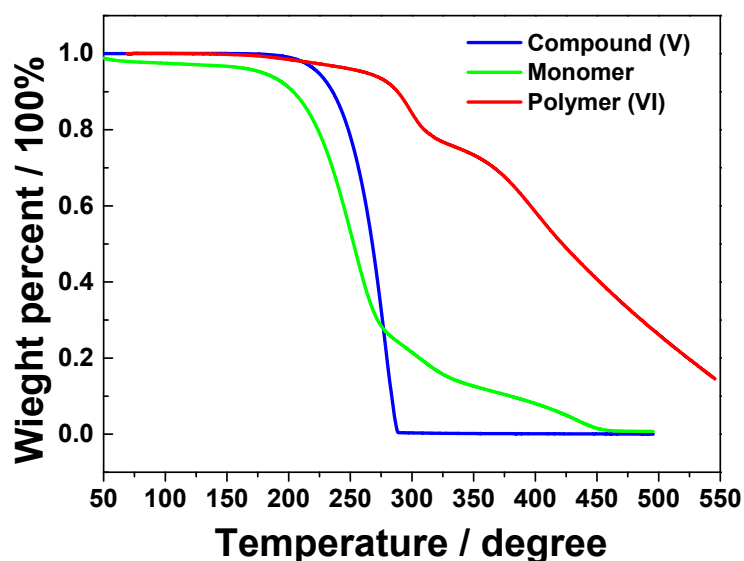


Figure S1. TGA diagrams of Compounds (V), monomer and polymer (VI).

4. Powder XRD

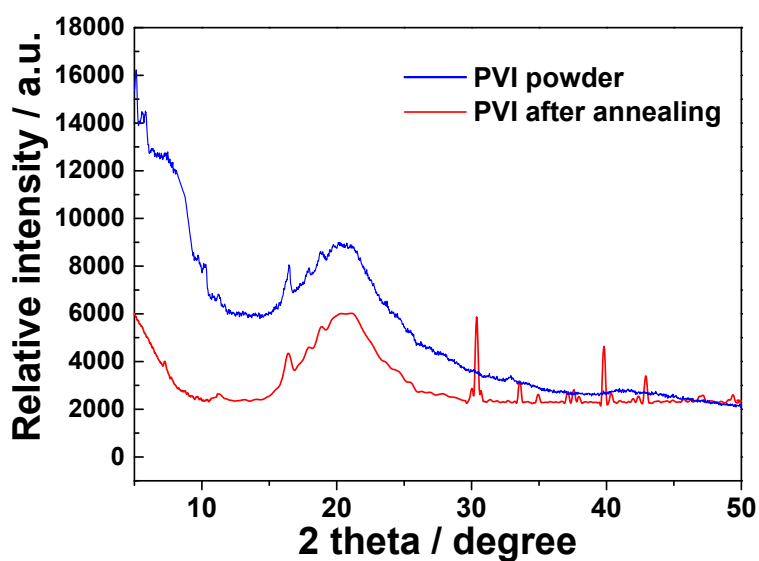


Figure S2. Powder X-ray diffraction (PXRD) patterns of polymer VI powder and thin film formed after annealing.

5. CV

The experiments were performed on a CHI instrument model 730B in a standard one compartment configuration equipped with three electrodes: Silver wire pseudo reference electrode, platinum wire counter electrode and glassy carbon working electrode. Glassy carbon electrodes were polished with alumina (1 μ m) prior to use. Chloroform was used as a solvent with 0.1 M of tetrabutylammonium hexafluorophosphate (TBAPF6) as a supporting electrolyte. The measurements were carried out at an analyte concentration of 1~2mg/mL with a scan rate of 0.1V/s. Ferrocene/ferrocenium (Fc/Fc⁺) couple was used as a calibration standard. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were obtained by correlating the oxidation and reduction onsets ($E_{\text{onset}}^{\text{ox}}$ and $E_{\text{onset}}^{\text{red}}$) to the Normal Hydrogen Electrode according to the following equations by assuming HOMO energy level of Fc/Fc⁺ to be -4.88 eV.

$$E_{\text{HOMO}} = -e(E_{\text{Onset}}^{\text{ox}} + 4.88)(\text{eV})$$

$$E_{\text{LUMO}} = -e(E_{\text{Onset}}^{\text{red}} + 4.88)(\text{eV})$$

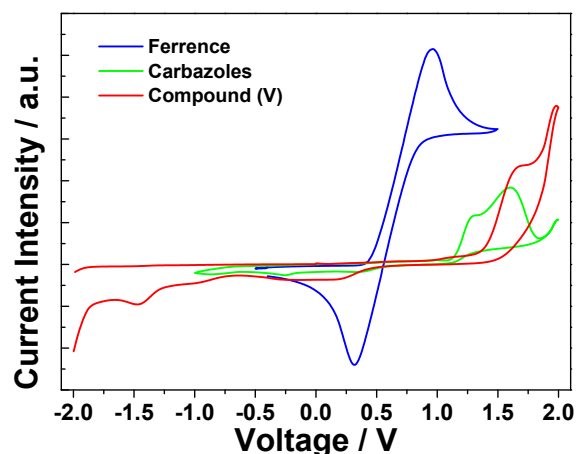


Figure S3. Cyclic voltammogram of ferrence as reference, carbazole and compound (V).

6. UV

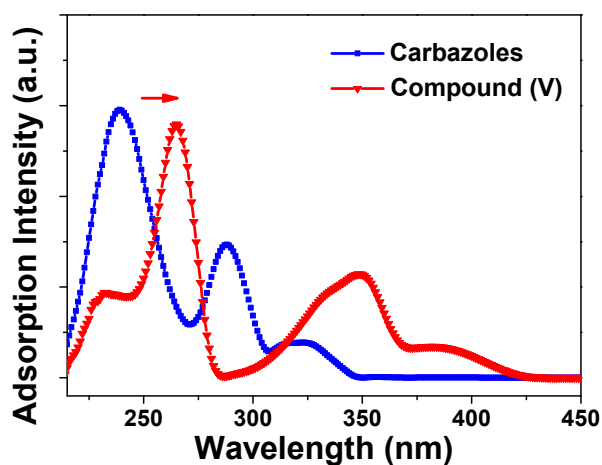


Figure S4. UV adsorption of carbazole and compound (V).

7. Polymerization of repeated units for polymer VI

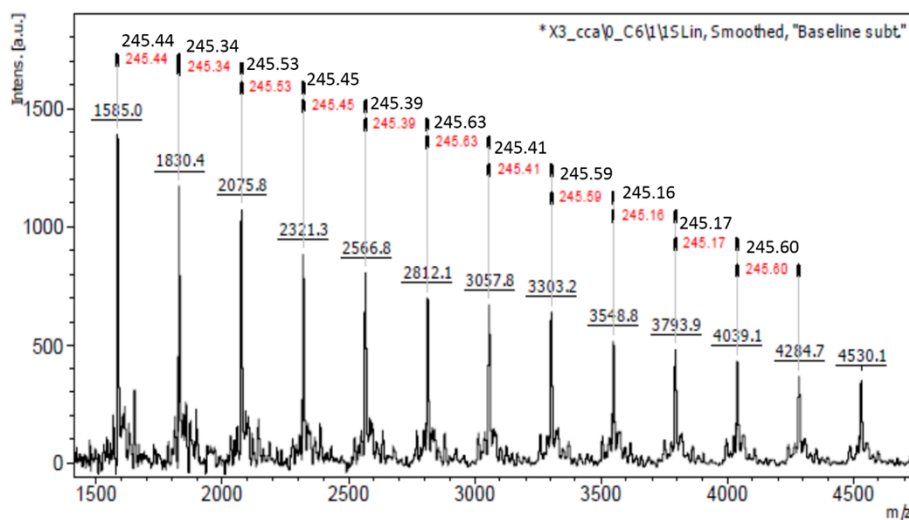
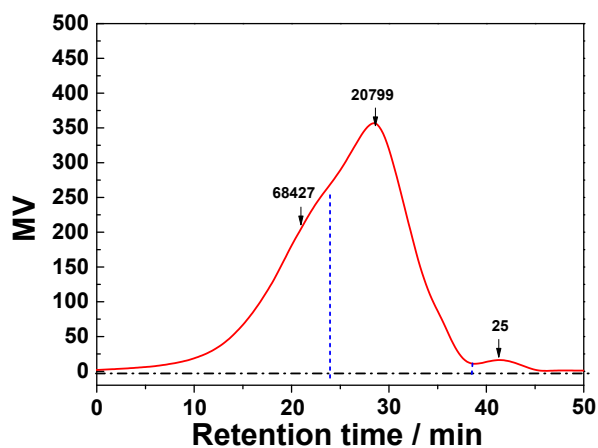


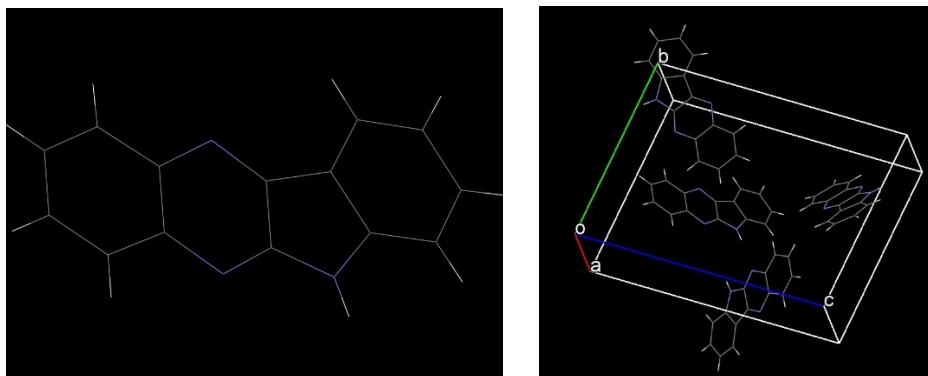
Figure S5. MALDI-TOF spectrum of the polymer (VI).



Sample	Retention time	Mn	Mw	Mp	Polydispersion (PDI)	Area%
1	20.234	27832	144987	68427	3.622	39
2	31.828	42432	71546	20799	1.832	58
3	42.732	20	23	25	1.124	3

Figure S6. GPC spectrum of the resulting polymer (VI) and summary table for all peaks observed.

8. Single crystal data of compound (V)



9. Charge carrier mobility

Organic field-effect transistors were fabricated in bottom gate, top contact configuration on heavily doped n-type Si substrates as the gate and thermally grown 200 nm silicon dioxide as the dielectric layer (Silicon Quest). Prior to deposition, devices were cleaned in acetone and isopropanol and dried in an oven at 120 °C for 15 min, then exposed for 20 min to UV ozone. The devices were surface treated with decyltrichlorosilane (DTS) for 10 min by immersion in 1% (by volume) DTS in toluene. The devices were then cleaned by rinsing with toluene and dried under nitrogen flow followed by spin-coating of the molecules. Molecules were all dissolved in orthodichlorobenzene with a concentration of 5 mg/mL and spin cast onto DTS-treated SiO₂/Si substrates at a spin rate of 3000 rpm. The source and drain electrodes were patterned using standard photolithography and were formed with e-beam evaporation of 3 nm nickel and 47 nm gold. The channel length (L) and channel width (W) were 20 μm and 1000 μm, respectively. Electrical characterization was performed using Keithley 4200 semiconductor characterization system.

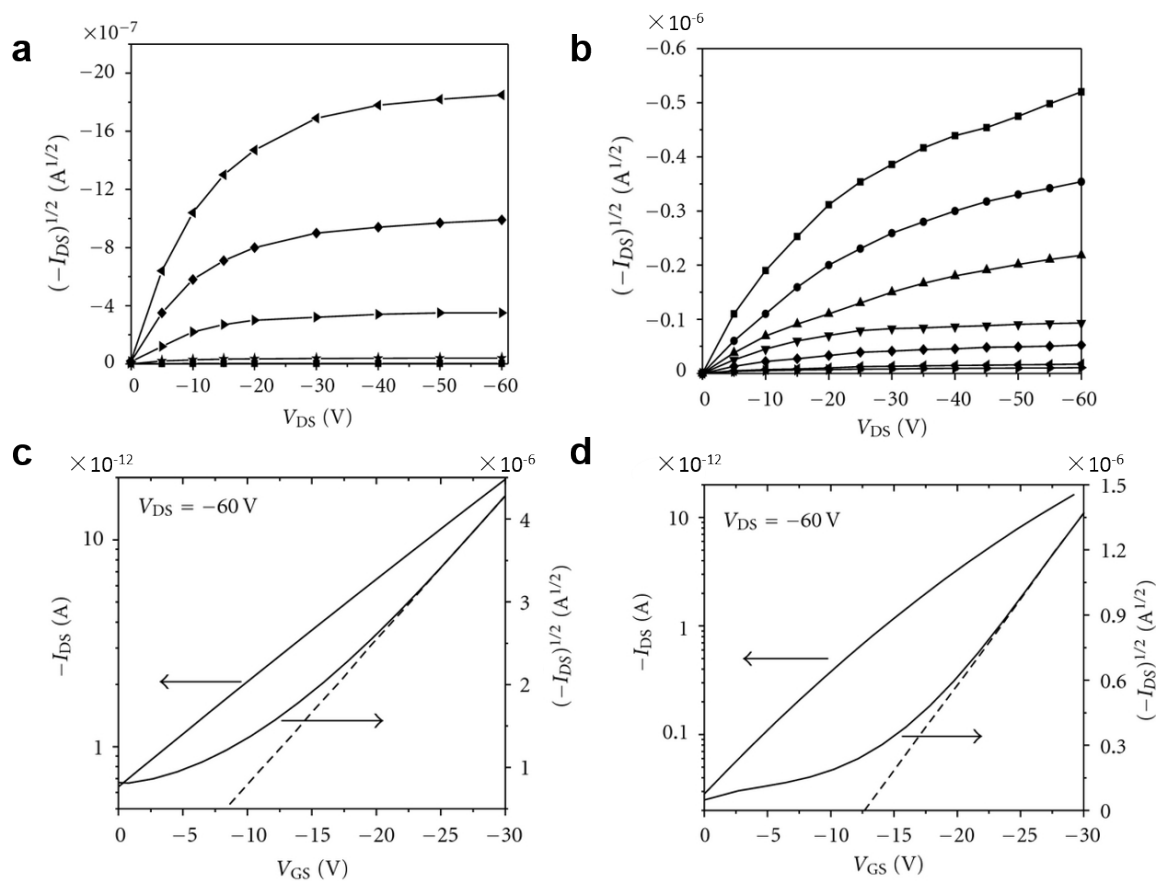


Figure S7. The square root of drain current ($I_D^{1/2}$), versus drain voltage (V_D) as a function of gate voltage (V_G), for an OFET device with thin film formed (a) from heat-treated PVI (VI), and (b) from heat-treated PVK precursors. Channel width of 5 mm and channel length of 100 μm were defined by gold source and drain electrodes. The V_G is from -60V to 0V (from bottom to top). (c) and (d) are plots of I_D versus V_G for $V_D = -60V$ and $I_D^{1/2}$ versus V_G in the saturation regime for the devices in (a) and (b).

10. Space Charge Limited Current (SCLC) Measurements

ITO glass slides were used as the substrates. Under the protection of Magic tape, the ITO films were patterned

by etching with aqua regia vapor. The patterned ITO glass substrates were cleaned in an ultrasonic bath sequentially by hot detergent, water, deionized water, toluene, acetone, and isopropyl alcohol, and then dried by compressed air. The cleaned ITO substrates were treated with UV ozone for 15 min before use. A highly conductive poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS; Heraeus Precious Metals; Clevios P VP AI4083) thin layer was spin-coated (5000 RPM, 30 s) onto the ITO substrates from an aqueous solution. The PEDOT:PSS thin films were dried at 120 °C on a hotplate in air for 5 min. The solutions of PVK and PVI were prepared in chlorobenzene with concentration of 20 mg mL⁻¹. The above solutions were spin-coated (once) on top of the PEDOT:PSS layers at 600 RPM for 30 s. The devices were transferred to glove box, and half of them were thermally annealed (once) one by one at 120 °C in the dark for 10 min. Subsequently, electrodes composed of 10 nm thick MoO₃ and 100 nm thick Al were deposited on the top by thermal evaporation under high vacuum (< 2 × 10⁻⁶ mb) through a shadow mask. 0.1 cm² active area of the devices was defined by the overlapped area of the ITO and the deposited MoO₃/Al electrodes. Current–voltage characteristics of the devices were measured using a Keithley 2400 source meter in the dark. The thickness of the films was measured with a Tencor Alphastep 200 automatic step profiler. The J–V characteristics of the hole-only devices are shown in Fig. S8.

Assuming contacts to be ohmic, the hole mobilities in the thin films can be obtained by fitting these J–V curves in the SCLC region using the following equation:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{(V_{app} - V_{bi})^2}{d^3}$$

where J is the current density in the SCLC region, V_{app} is the applied voltage, V_{bi} is the built-in voltage, ε_0 is the permittivity of free space (8.854 × 10⁻¹² F m⁻¹), ε_r is the relative dielectric constant of the thin film which is assumed to be 3 (a typical value for an organic semiconductor), μ is the charge carrier mobility, and d is the thickness of the thin film. From the presented curves, we can find that the PVI based device provides higher current density under same applied voltages. It further indicates that PVI has better hole transporting ability, and the hole transport for PVI based device is more efficient as compared with that of PVK based device.

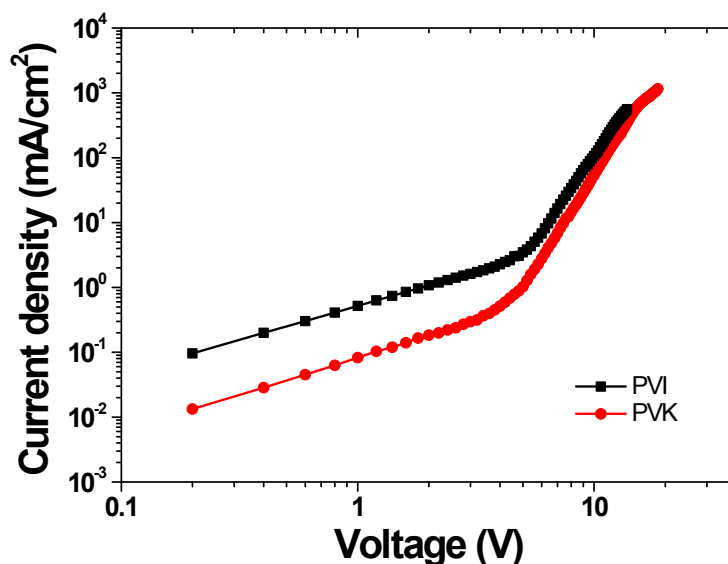
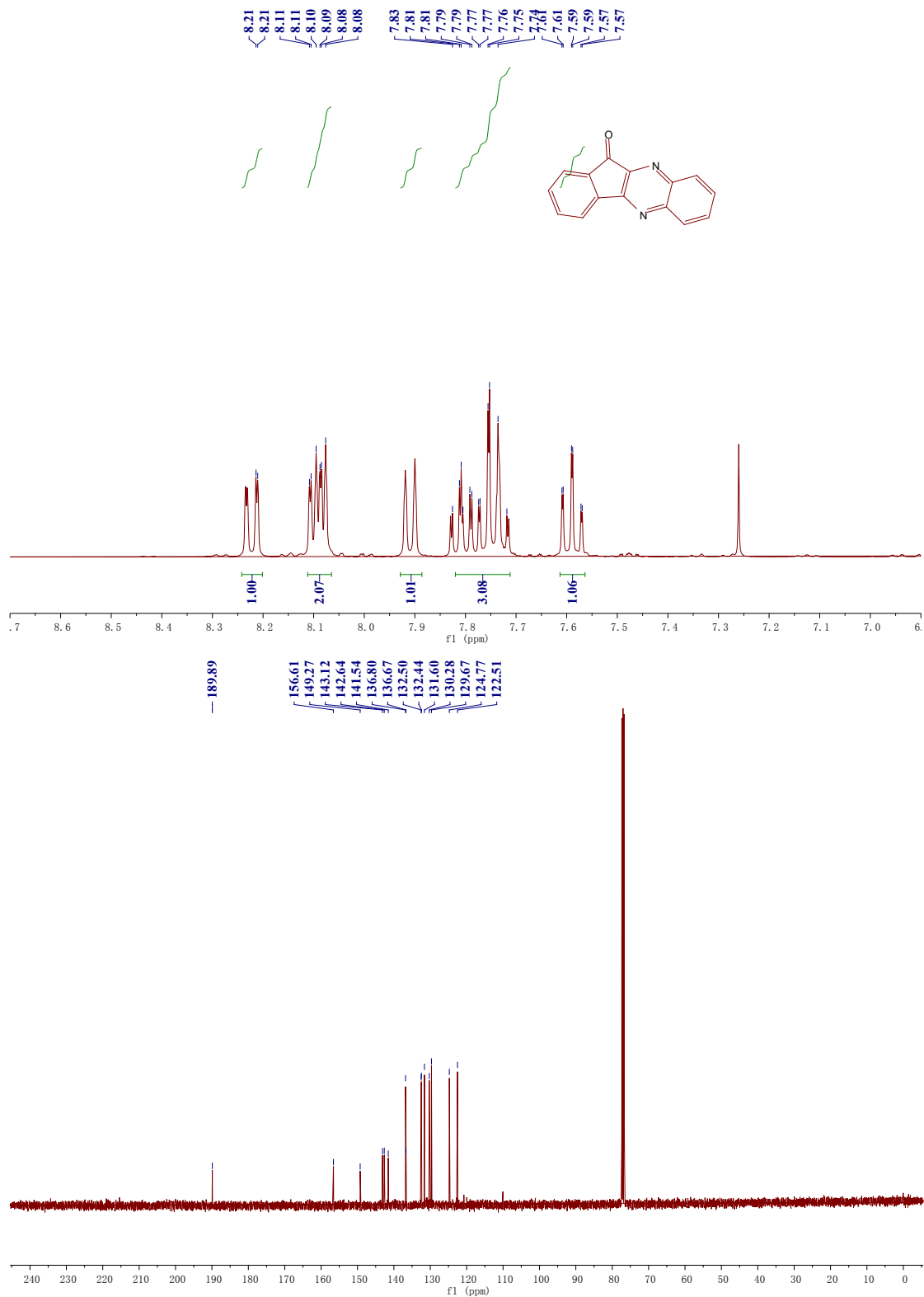


Figure S8. Experimental current density–voltage characteristics of the highest-performing hole-only devices using thin films of PVI (VI) and PVK with the configuration of ITO/PEDOT:PSS/HTL/MoO₃/Al under thermal annealing.

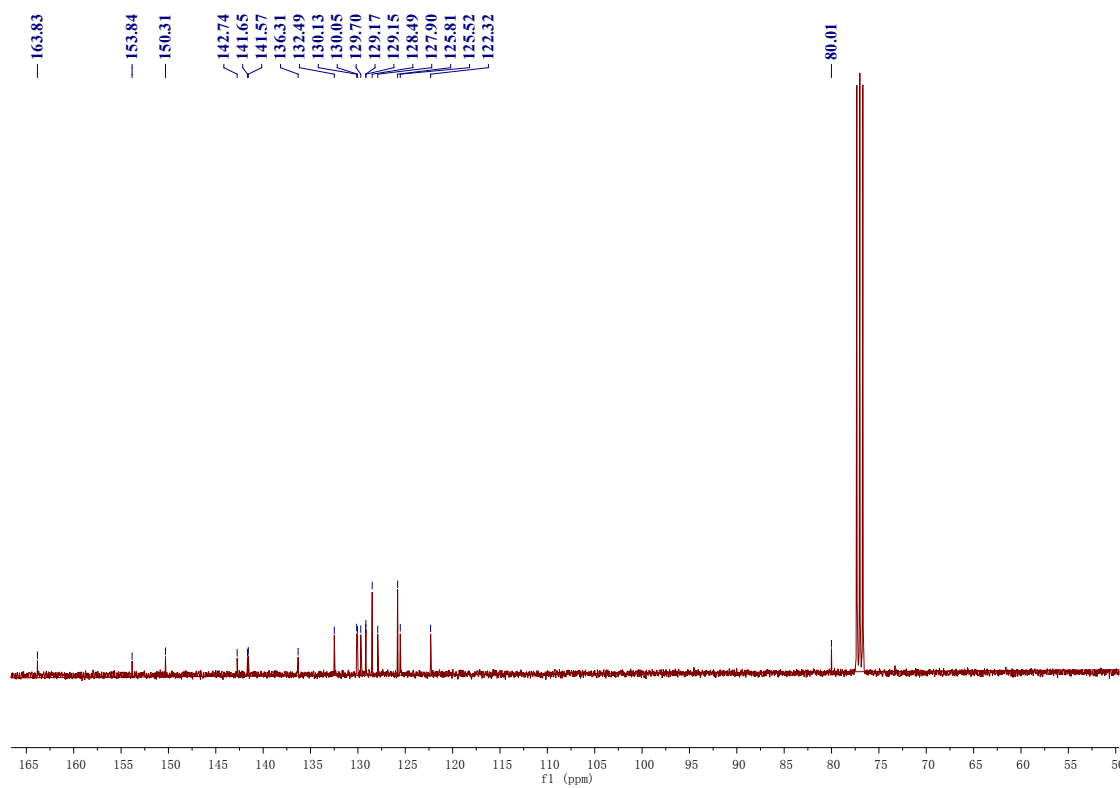
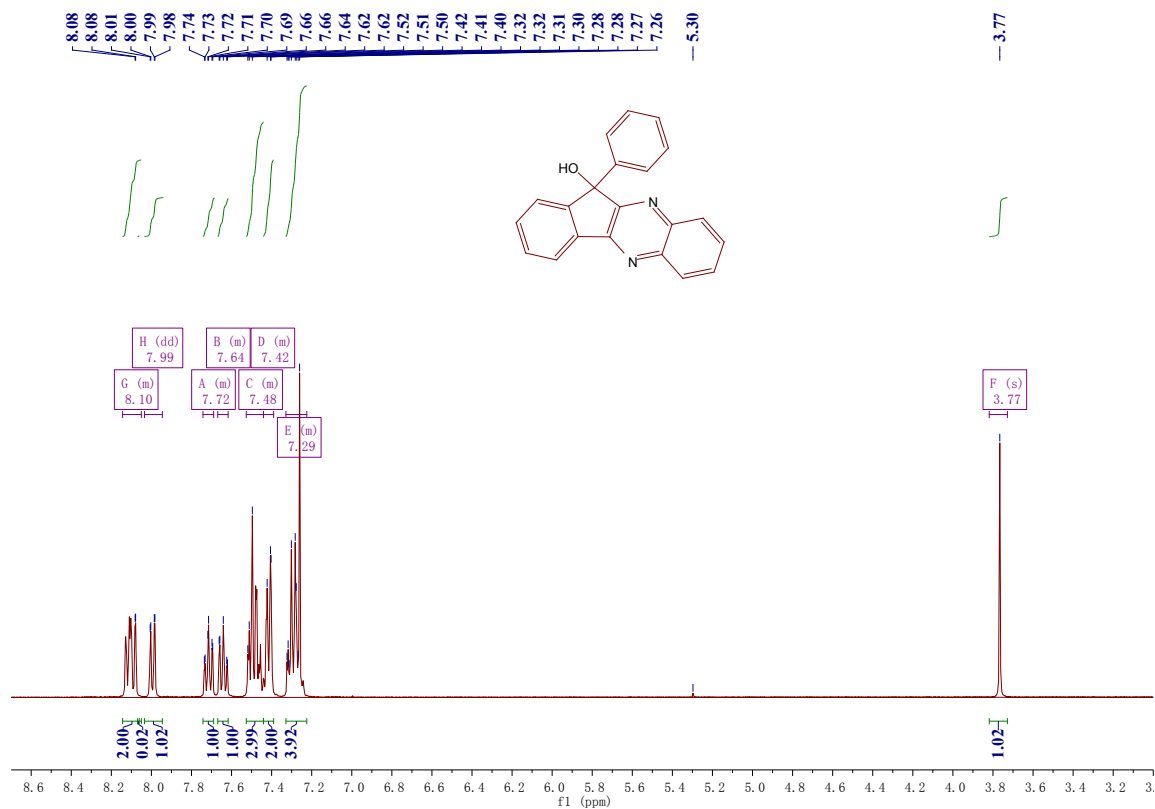
Appendix

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

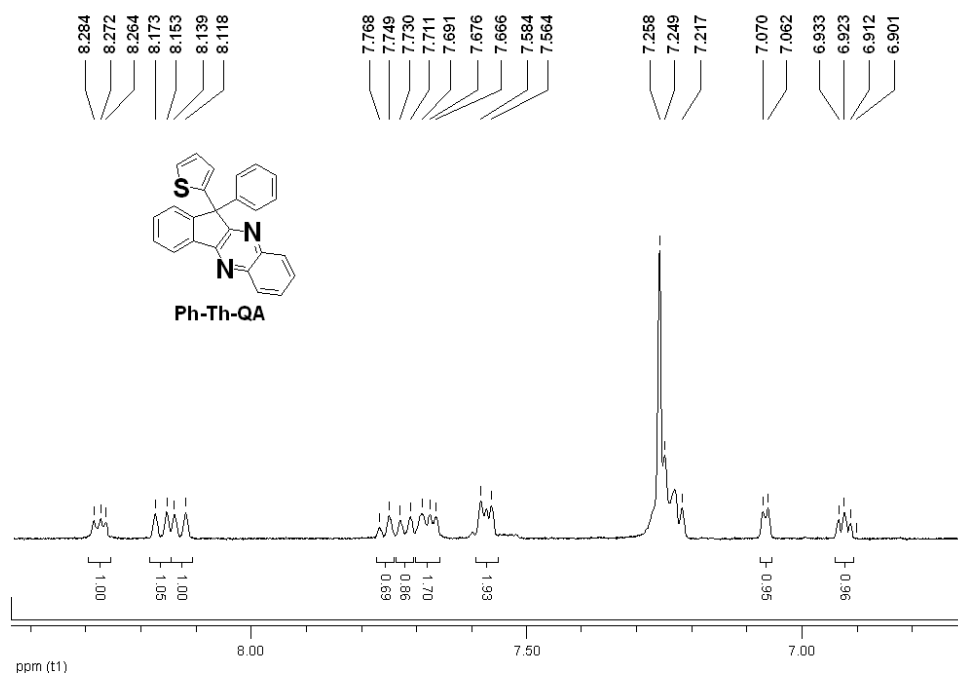
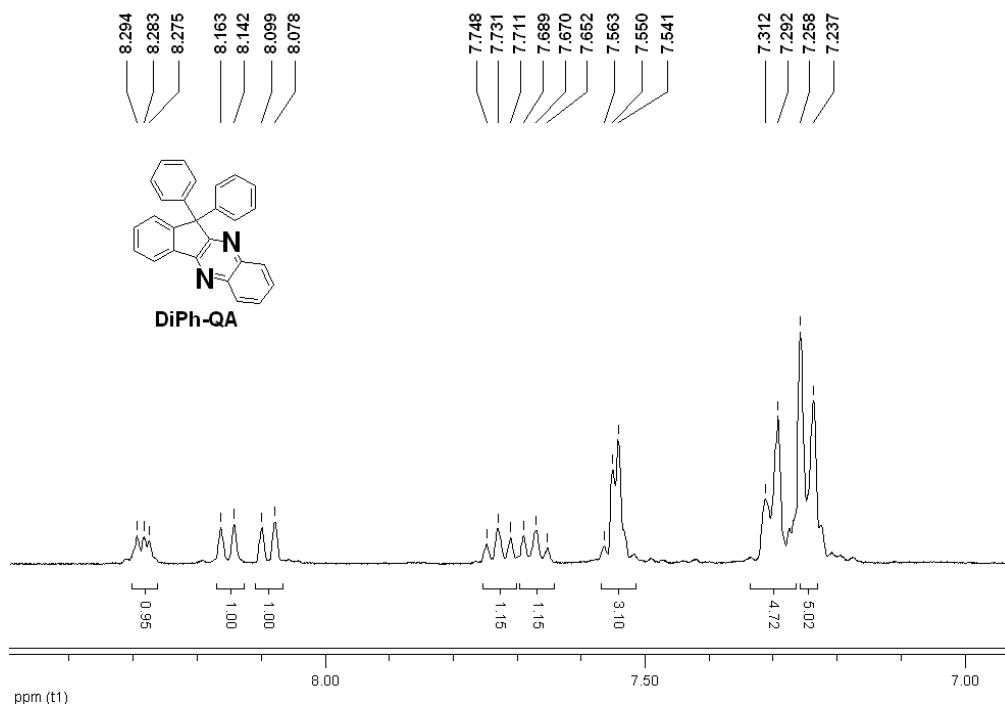
1.1 Compound (I)



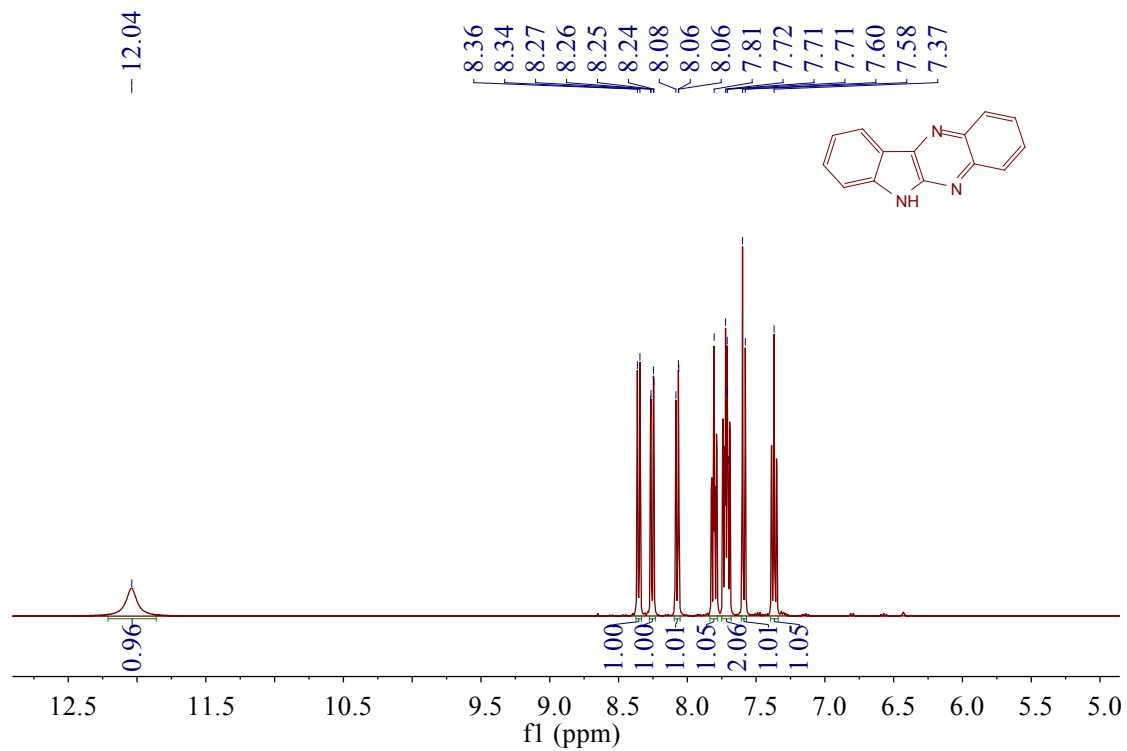
1.2 Compound (II)



1.3 Compounds (III and IV)

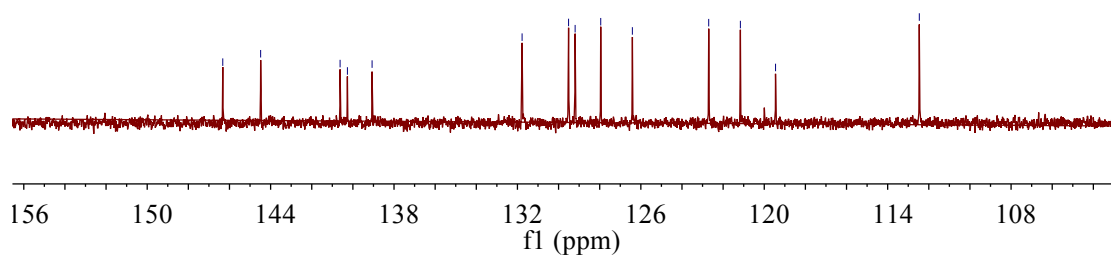


1.4 Compound (V)

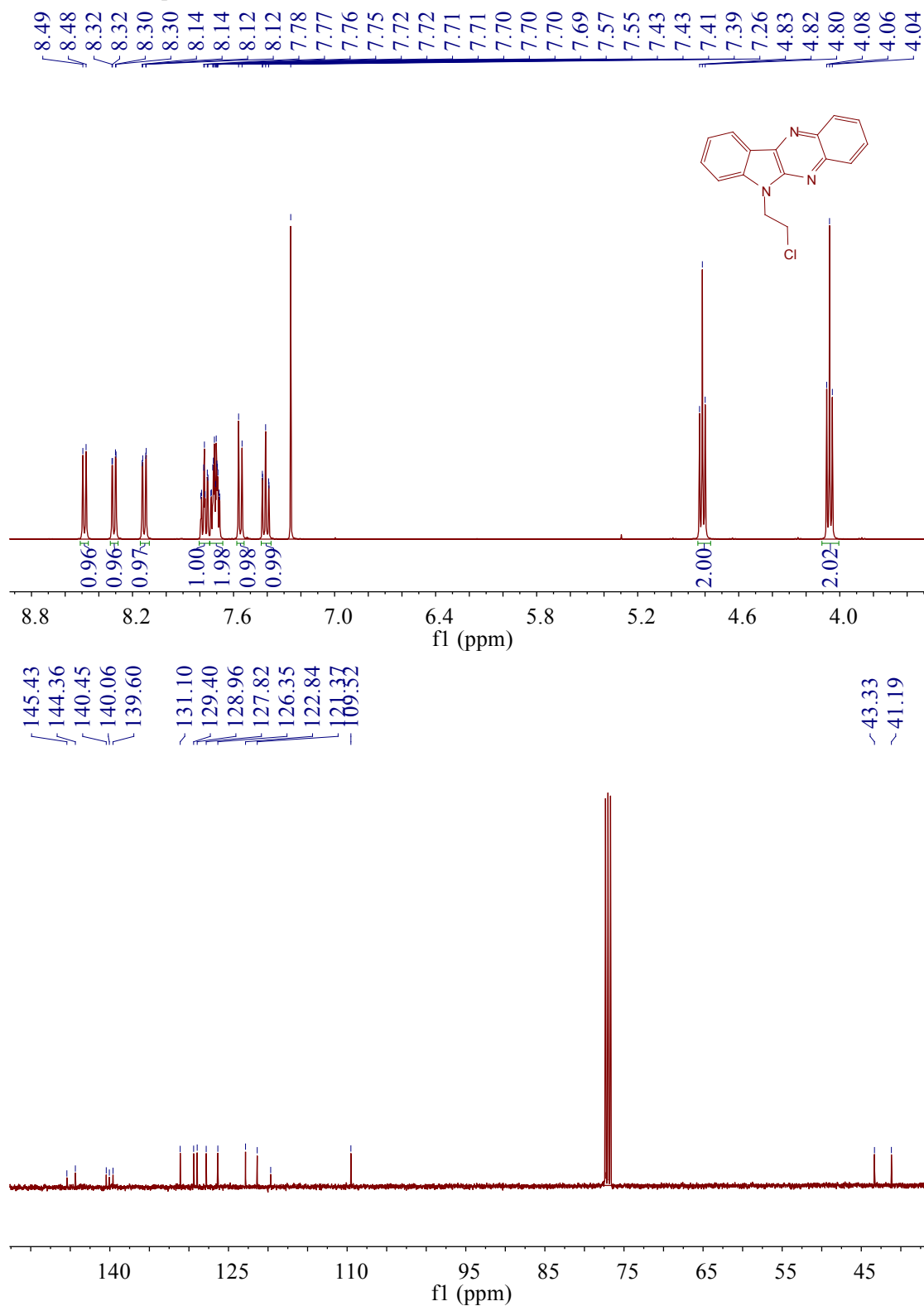


YBK-NH
YBK-NH, DMSO, BBF0400

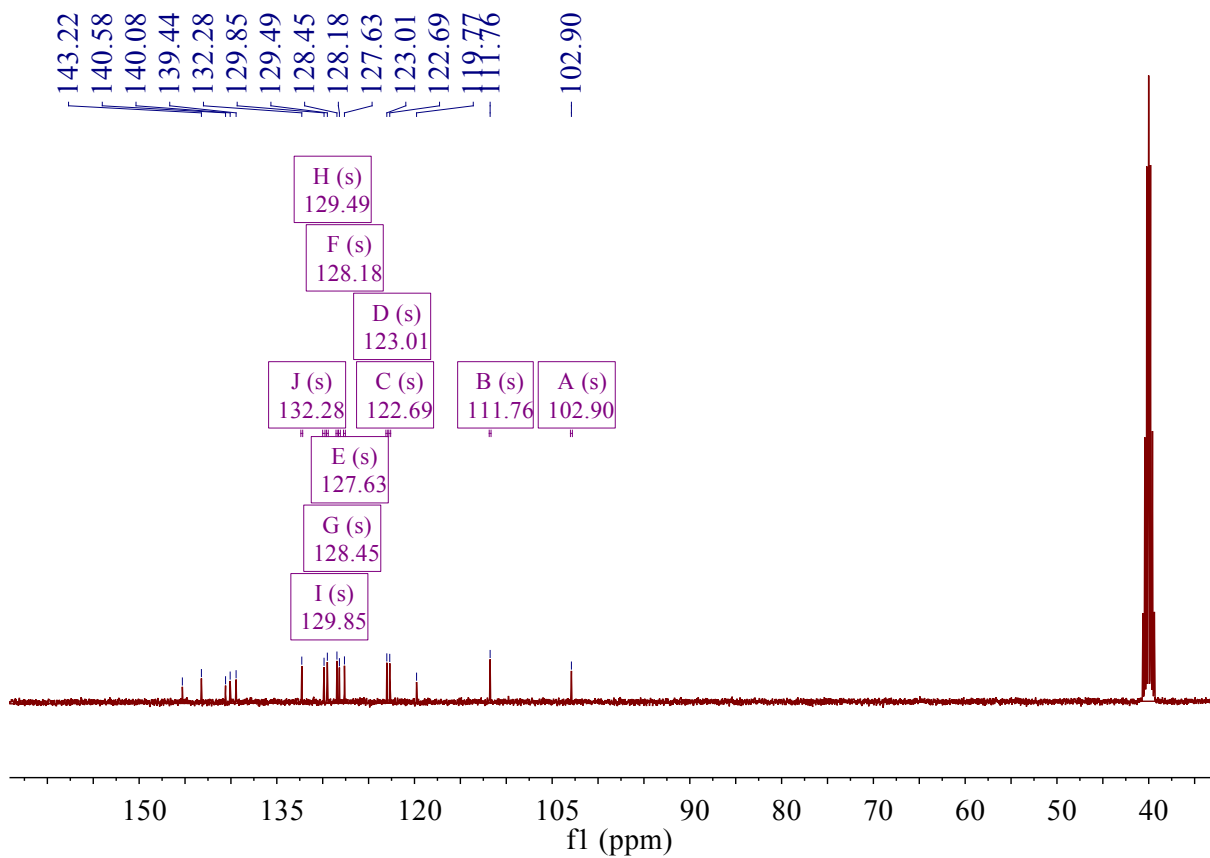
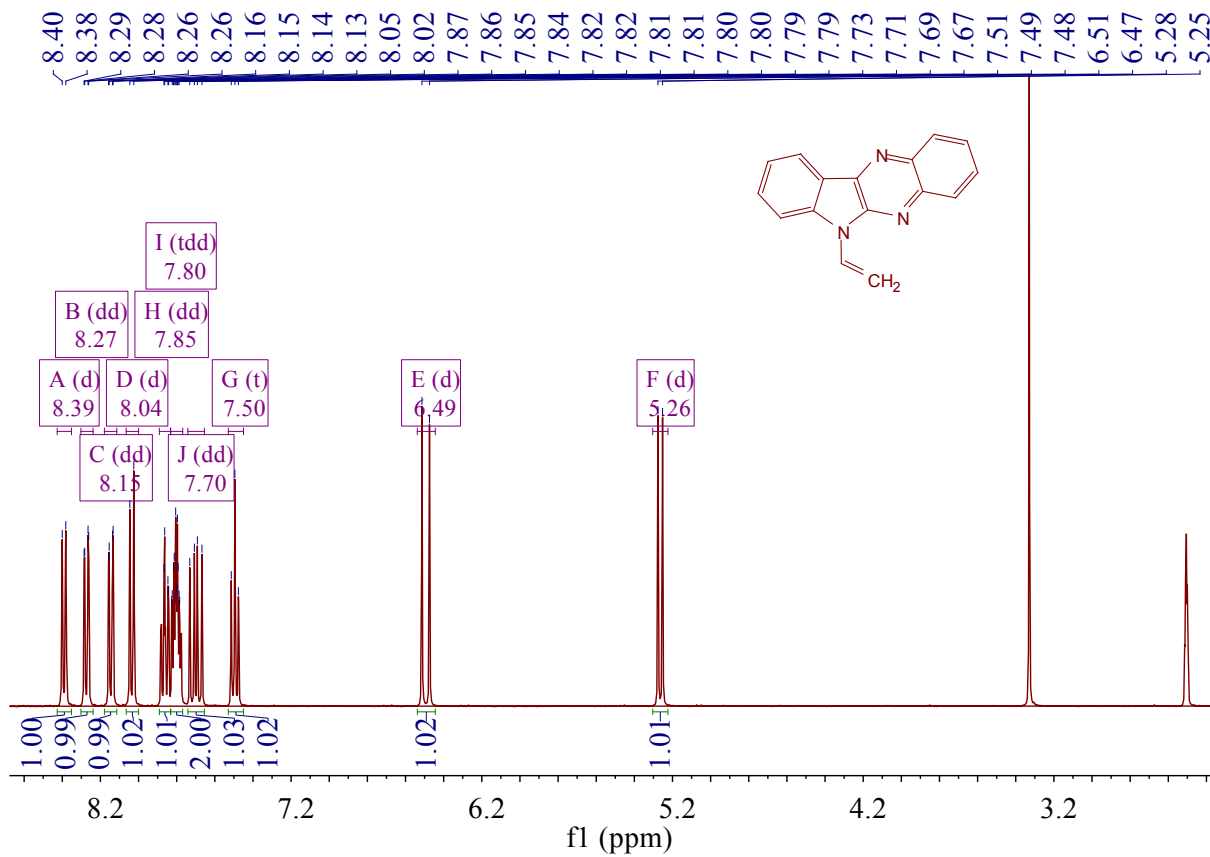
146.33
144.48
140.62
140.27
139.07
131.77
129.51
129.19
127.95
126.41
122.70
121.16
119.45
112.46



1.5 Intermedia product



1.6 Monomer



2. MS spectra
 2.1 Compound (I)

Elemental Composition Report

Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass: Even Electron Ions

57 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

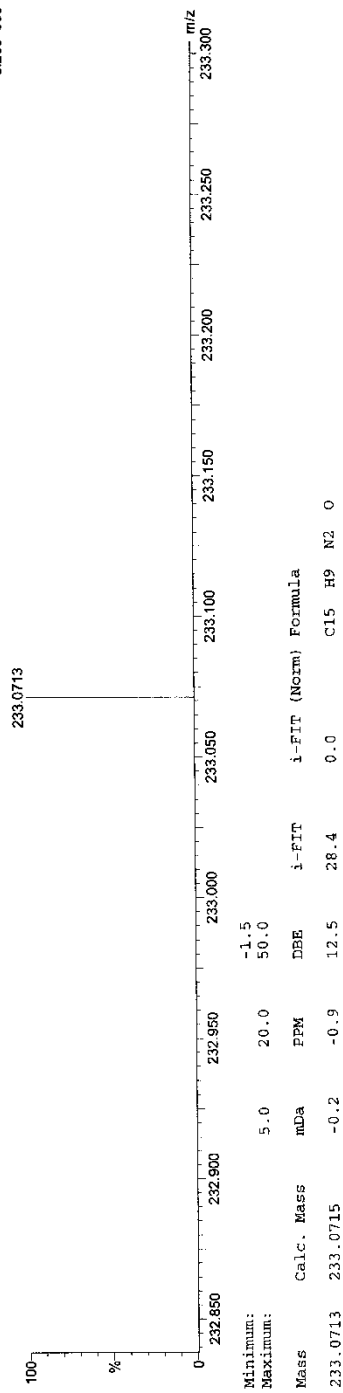
Elements Used:

C: 0-22 H: 0-29 N: 0-2 O: 0-6

C15H8N2O

YBK 6 (0.138) Cm (6:14)

1: TOF MS ES+
 8.29e+003



2.2 Compound (II)

Elemental Composition Report

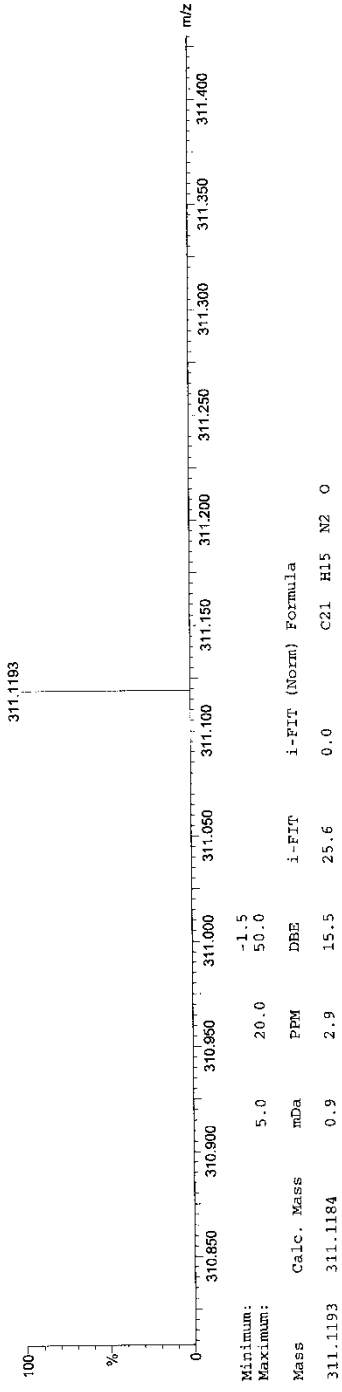
Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
21 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:
C: 21-22 H: 0-29 N: 0-2 O: 0-6
C₂₁H₁₄N₂O
YBKc-Ph-OH 8 (0.175) Cm (8:16)

1: TOF MS ES+
2.11e+003



2.3 Compound (V)

Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
 Element prediction: Off
 Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
 11 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

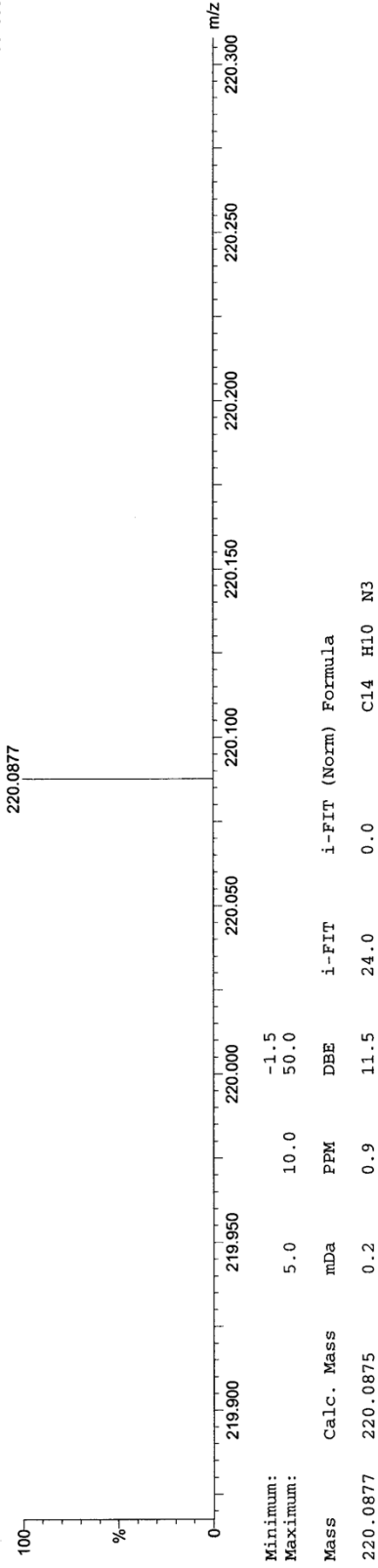
Elements Used:

C: 0-24 H: 0-33 N: 0-3

C14H9N3

YBK-NH 8 (0.175) Cm (8)

1: TOF MS ES+
 1.43e+003



Minimum:
 Maximum:

-1.5
 50.0

Elemental Composition Report

Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

18 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

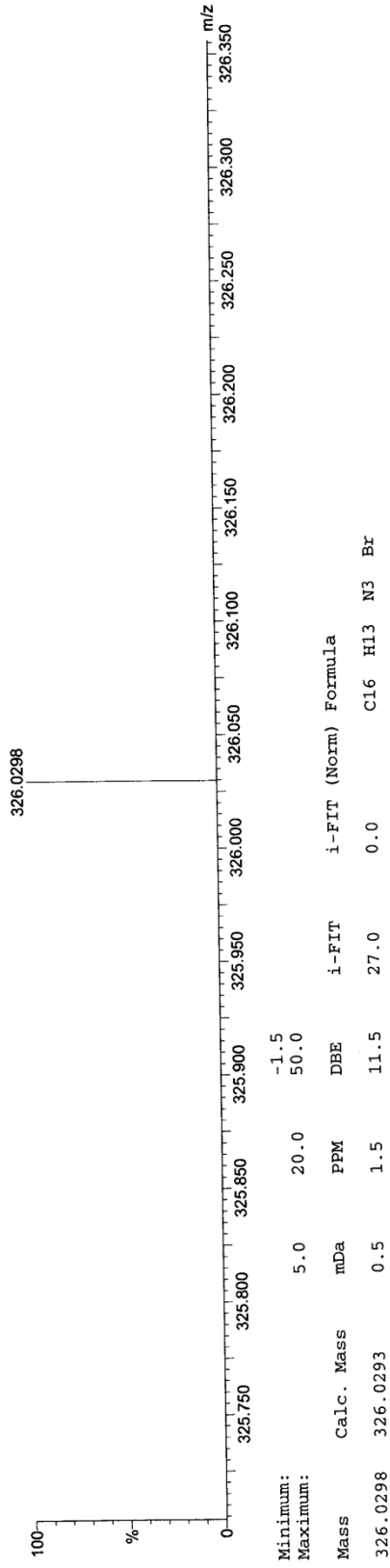
Elements Used:

C: 0-22 H: 0-29 N: 0-4 Br: 0-1

C16H12N3Br

YBK-NH-Br-9 (0.220) Cm (9:16)

1: TOF MS ES+
2.60e+003



2.5 Polymer (VI)

