

Synthesis, characterization and electrochemistry of polycyclic fused aromatic pyrroles and their conjugated polymers

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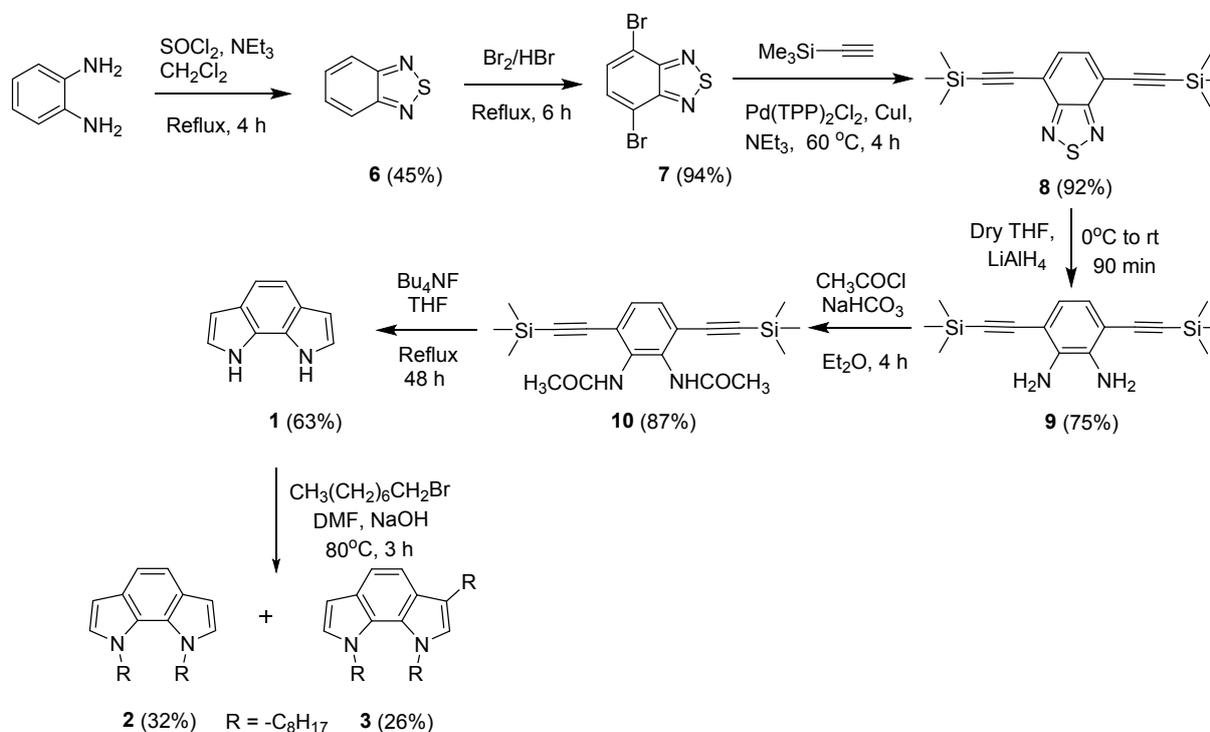
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General procedures: All the chemicals were reagent grade and used as purchased. Moisture-sensitive reactions were performed under an inert atmosphere of dry nitrogen with dried solvents. Reactions were monitored by thin-layer analysis (TLC) analysis using Merck 60 F₂₅₄ aluminium-coated plates and the spots were visualized under ultraviolet (UV) light. Column chromatography was carried out on silica gel (60–120 mesh). Mass spectra were recorded on Thermo-Fischer DSQ II GCMS instrument. NMR spectra were recorded on a Bruker Avance-III 400 spectrometer in CDCl₃ and DMSO-D₆. UV-Visible absorption spectra were recorded on Jasco V-630 spectrophotometer using quartz cuvette. CV data were obtained with CH Instruments model of CHI 600C with three electrode (Pt disc/glassy carbon as the working electrode, platinum as the counter electrode, and nonaqueous Ag/AgNO₃ as the reference electrode) cells in anhydrous acetonitrile/THF solution containing 50 mM tetra-n-butylammonium hexafluorophosphate (TBAPF₆) at a scan rate of 100 mV/s under an N₂ atmosphere. The redox onset potential of ferrocene/ferrocene⁺ $E_{onset}(Fc/Fc^+)$ under the same conditions is recorded. The HOMO levels were calculated by using the equation: $E_{HOMO} = -(E_{ox,onset} + 4.8 - E_{onset}(Fc/Fc^+)) eV$. Tapping mode atom force microscopy (TM) Gel permeation chromatography was performed over Resipore/PLgel 5 μm Mixed-C column at 40°C temperature, using THF as eluent at a flow rate of 1-2 mL/min taking polystyrene as a standard. Thermo-Gravimetric Analysis (TGA) of the polymer was done on Exstar SII TG/DTA 6300 using N₂ as inert gas. Differential Scanning Calorimetry (DSC) of the polymer was performed with Mattler Toledo DSC822^e under N₂ atmosphere. The conductivity was measured using Solartron 1287 electrochemical interface and 1260 impedance gain phase analyzer interface by placing the active material between two stainless steel electrodes waving over a frequency range of 1.2 MHz to 0.1 Hz with 10 mV AC amplitude at 25 °C.

Synthesis and characterization of intermediate compounds 6, 7, 8, 9 and 10

Intermediate compounds **6**, **7** and **8** were synthesized according to the literature¹. Compound **9** was synthesized according to the method reported by Lindner et al². Compound **10** was synthesized by N-acylation reaction of compound **9** using acetyl chloride and sodium bicarbonate as a mild base in dry diethylether at 0°C.



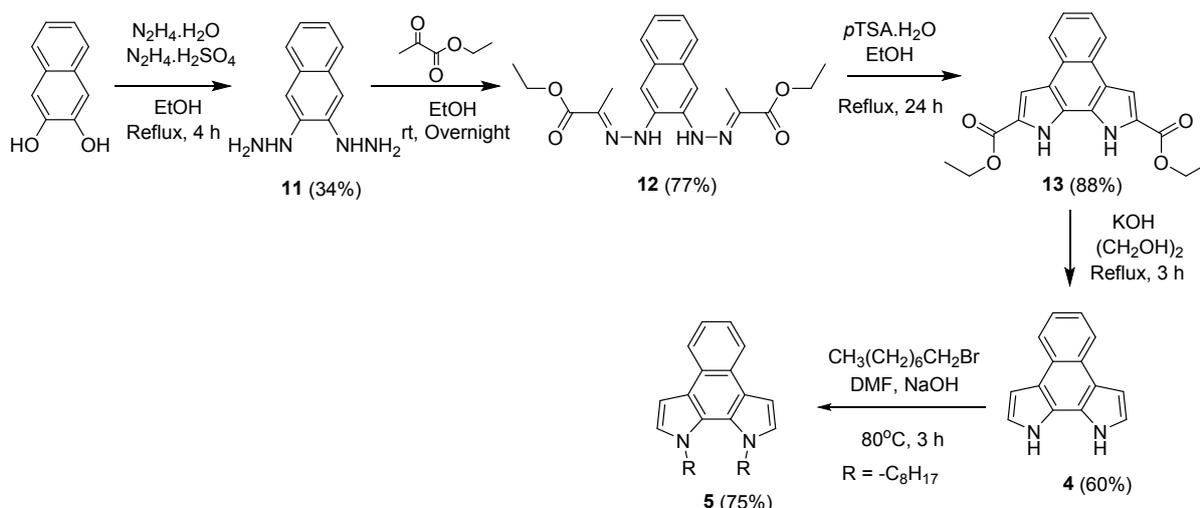
Scheme S 1 Synthesis of benzodipyrrole **1**, N,N'-dioctylbenzodipyrrole **2** and N,N'-diocyl-3-octylbenzodipyrrole **3**

1, 4-diamino-2, 5-bis(trimethylsilylethynyl)benzene **9** was synthesized by the method reported by Lindner et al². 4, 7-Bis(trimethylsilylethynyl)-2, 1, 3-benzothiadiazole **4** (100 mg, 0.304 mmol) was dissolved in THF (5 mL) in a heatgun-dried Schlenk-tube under nitrogen. LiAlH₄ (0.058 g, 1.52 mmol) was added slowly over 5 min at 0°C. After stirring for 90 min at room temperature the mixture was cooled down to 0°C again and treated with a saturated NH₄Cl-solution. The mixture was diluted with water (30 mL) and extracted three times with EtOAc (30 mL). The combined organic layers were dried over Na₂SO₄ and evaporated. The crude product was subjected directly for the di-acetyl protection of obtained di-amine.

N,N'-(3,6-bis(trimethylsilylethynyl)-1,2-phenylene)diacetamide **10** was synthesized as below. The crude 1, 4-diamino-2, 5-bis(trimethylsilylethynyl)benzene **9** (1.000 gm, 3.32 mmol) was dissolved in dry Et₂O (20 mL). To this was added anhydrous sodium bicarbonate (1.399 gm, 16.64 mol) and the resulting suspension was stirred at 0°C for 10 minutes. To this cooled suspension was added acetyl chloride (0.785 gm, 9.98 mmol), dropwise over a period of 5 min. After complete addition the reaction mixture was stirred for 4 h at room temperature and quenched with water (30 mL). Organic layer was separated and aqueous layer was again extracted twice with DCM. Combined organic layer is washed with saturated brine solution and finally with water, dried over MgSO₄ and evaporated to dryness to yield pale yellow powder. Further purification was achieved by washing crude product with copious amounts of n-hexane, yielding white product. ¹H NMR (400 MHz, CDCl₃): 7.91 (s, 2H), 7.35 (s, 2H), 2.20 (s, 3H), 0.27 (s, 9H). ESI-MS 384.04 [M⁺] (62%), 325.22 [M-59(-NHCOCH₃)] (30%).

Synthesis of intermediate compounds **11**, **12** and **13**

Naphthobipyrrole **4** is a known compound³ and was synthesized as shown in scheme S 2 using the modification of the literature procedure reported by Roznyatovskiy et al⁴.



Scheme S 2 Synthesis of naphthobipyrrole **4** and N,N'-dioctylnaphthobipyrrole **5**

Compound **11** was synthesized according to the literature procedure reported by Franzen et al⁵. Compound **12** and **13** were prepared according to the literature procedure reported by Roznyatovskiy et al⁴.

Naphthalene-2,3-dihydrazine **11** was synthesized using a modified literature procedure reported by Franzen et al⁶. A two necked round bottom flask was charged with 2,3-dihydroxynaphthalene (6.00 gm, 37.50 mmol), 6 mL of hydrazine hydrate (99%) (6.18 gm, 123.60 mmol), hydrazine sulphate (2.00 gm, 15.38 mmol) and ethanol (2 mL). The solution

was refluxed until reaction mixture turned in to clear, red liquid. This clear liquid was refluxed for 4 h till slight precipitation began to appear. The reaction mixture was allowed to cool slowly to the room temperature during which time more solids precipitate out. To it, 40 mL DCM and 10 mL MeOH was added and solids were quickly filtered off using vacuum filtration, washed with 2X10 mL 8:2 DCM-MeOH and dried under vacuum to yield air sensitive off white product **1** in 60% yield (4.21 gm, 22.35 mmol). As being very unstable, crude product was directly taken for the synthesis of 2,3-(ethyl propanoate-2)-naphthelenehydrazone without any characterization.

2,3-(ethyl propanoate-2)-naphthelenehydrazone **12** was synthesized using a modified literature procedure reported by Roznyatovskiy et al⁴. To a 250 mL two-necked round bottom flask were added Naphthalene-2,3-dihydrazine **11** (4.21 gm, 22.35 mmol) and 56 mL of EtOH. To this was added solution of Ethyl Pyruvate (6.50 gm, 56 mmol) in 5.6 mL of EtOH, dropwise. During the addition, slight exothermicity was observed and yellow solids began to precipitate out. After complete addition, the reaction mixture was stirred at room temperature overnight. The light yellow reaction mixture slurry was filtered off and solids were washed with small amount of EtOH and dried under vacuum to yield light yellow product **12** as a mixture of two isomers (symmetrical and non-symmetrical) in 72% yield (6.20 gm, 16.15 mmol). This crude mixture was characterized by mass spectroscopy. ESI-MS 384.17 [M⁺] (58%). Rest of characterization data were reported by Roznyatovskiy et al⁴.

Diethyl-1,10-dihydrobenzo[e]pyrrolo[3,2-g]indole-2,9- dicarboxylate **13** was synthesized using literature procedure reported by Roznyatovskiy et al⁴. Dihydrazone **12** (3.00 gm, 7.81 mmol), tosic acid hydrate (14.84 gm, 78.12 mmol) and EtOH (0.1 M, 78 mL) were charged in a two necked round bottom flask and heated to reflux for 3 h. After completion of reaction as indicated by TLC, reaction mixture was allowed to cool at room temperature during which the product precipitated out. The product was filtered off using vacuum filtration, washed with small amount of EtOH, and dried under vacuum, yielding bluish white product **13** in 80% yield (2.20 gm, 6.29 mmol). ¹H NMR (400 MHz, DMSO-D₆): 11.89 (s, 2H), 8.32-8.34 (dd, J₁=6 Hz; J₂= 2.4 Hz, 2H), 7.83-7.84 (d, J = 2.4 Hz, 2H), 7.46-7.48 (dd, J₁=6 Hz; J₂= 2.4 Hz, 2H), 4.36-4.41 (q, J= 6.8 Hz, 2H), 1.37-1.40 (t, J=7.2 Hz, 3H). ESI-MS 350.16 [M⁺] (67%), 349.16 [M-1] (66%). All other characterization data were reported in literature⁴.

Cyclic voltammograms of compounds 1, 2, 3, 4 and 5

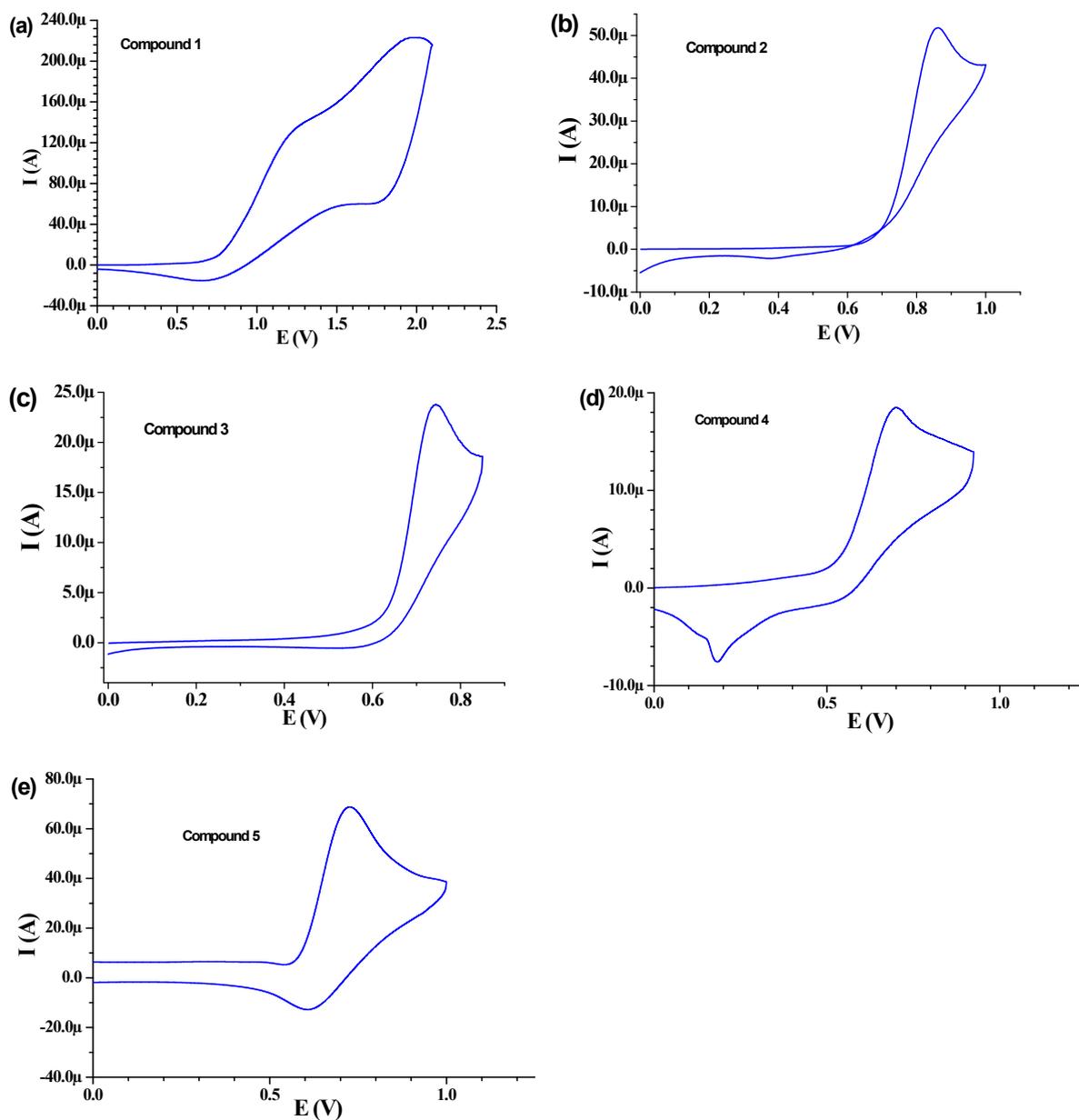


Figure S 1 Cyclic voltammetry of compounds 1, 2, 3, 4 and 5 in acetonitrile (~ 5 mM) using TBAPF₆ as supporting electrolyte (~ 50 mM) cycled at 50 mV/s on Pt disc electrode.

Electrochemical polymerization of compounds 1, 2, 4 and 5

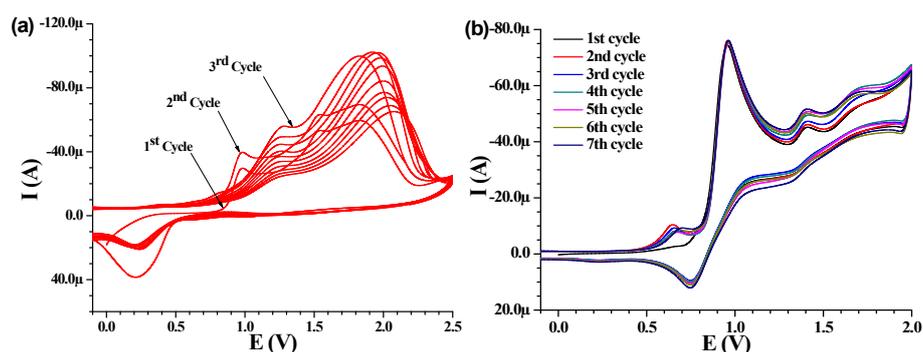


Figure S 2 Electro-chemical polymerization of (a) compound 2 (b) compound 5, (~5 mM) at 50 mV/s in acetonitrile using TBAPF₆ (~50 mM) as supporting electrolyte on Pt disc electrode.

Compounds 1, 2, 4 and 5 were electro-chemically polymerized using a three electrode cell comprising Pt-disc working electrode, Pt-wire counter electrode and a Ag/Ag⁺ reference electrode. The monomers were dissolved in dry acetonitrile (~ 5 mM) along with TBAPF₆ as a supporting electrolyte and were scanned for repeated CV cycles to see the electro-chemical polymerization ability of the monomers at applied anodic potentials. Compounds 1, 2, 4 and 5 polymerized irreversibly with the applied oxidation potentials (Figure S 2).

The compound 1 was scanned between +2.11 V to -0.20 V at 50 mV/s however subsequent cycling between -0.20 V to +2.11 V surprisingly did not yielded any polymeric deposits on Pt disc electrode and in CV data, no increase in the current intensity was observed which may be attributed to the deposition of electro-active material on Pt disc electrode. Instead, black polymeric particles were observed precipitating out inside the solution. So we concluded that BDP is getting oxidized by the applied voltage but somehow it is not forming electro-active polymeric layer on Pt disc electrode. Another possible reason for not getting electro-active polymer layer on the working electrode might be the active involvement of both α - and β -pyrrolic positions in the polymerization, i.e., when compound 1 is oxidized by applying the voltage, polymer formation occurs by the both α - α' and β - β' linkage, resulting in to the branched polymer with irregularities rather forming a linear polymer.

The compound 2 was scanned between +2.50 V to -0.20 V at 50 mV/s for 12 cycles, as shown in the Figure S 2a; during the 1st and 2nd cycles, current intensity of the oxidation peaks with anodic peak potential +0.99 V and +1.82 V increases. From the 3rd cycle, anodic peak potential of the first oxidation peak shifts anodically from +0.99 V to +1.28 V, with the

increase in the current intensity. 4th cycle onwards, current intensity of both the oxidation peaks decreases continuously, accompanied by the disappearance of the first oxidation peak with anodic peak potential +1.28 V and anodic shift of the peak potential of the second oxidation peak from +1.82 V to +2.05 V. However, the continuous polymeric films which coat the electrode surface evenly are not obtained which can be explained by the stability of the cationic intermediates, i.e., the cationic intermediates which are produced on the electrode surface are being sufficiently stable to diffuse away from the electrode rather than being captured by another molecule of compound **2** to generate polymeric film on the electrode⁷. This explanation is also supported by the photography of the ongoing electro-chemical polymerization of compound **2** (Figure S 3) which is showing diffusion of the oligomeric intermediates from the working electrode in to the solution.

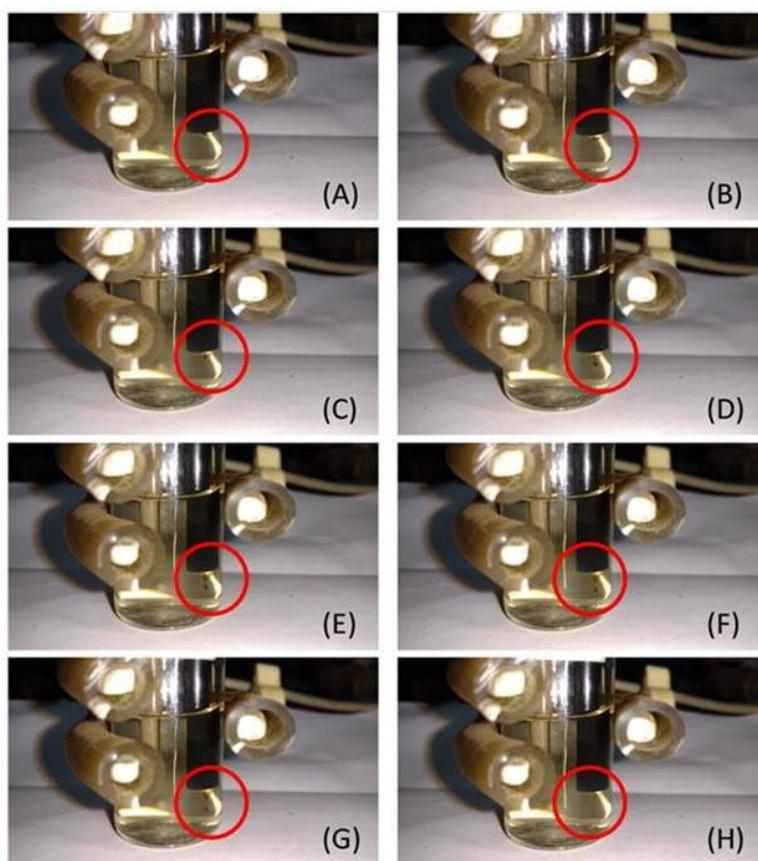


Figure S 3 Photographs of electro-chemical polymerization of compound **2** showing diffusion of the polymer being formed on the working electrode surface in to the electrolytic solution.

Compound **5** was subjected to the electro-chemical polymerization in dry acetonitrile (~5 mM) along with TBAPF₆ (~50 mM) as a supporting electrolyte at a scan rate of 50 mV/s using cyclic-voltammetry (Figure S 2b). Subsequent cycling between +2.00 V to -0.20 V

yielded polymeric deposits on Pt disc electrode and in the cyclic voltammetric data, current intensity of the second oxidation peak at +1.41 V increases gradually which may be attributed to the deposition of electro-active material on Pt disc electrode. Also, after the 1st cycle, an additional oxidation peak developed at the anodic peak potential +0.64 V which can be explained as the oxidation of polymer film being formed on the working electrode. However, it was noted that during the electro-chemical polymerization experiment, the polymer formed on the surface of the working electrode was being diffused again in to the electrolytic solution (Figure S 4).

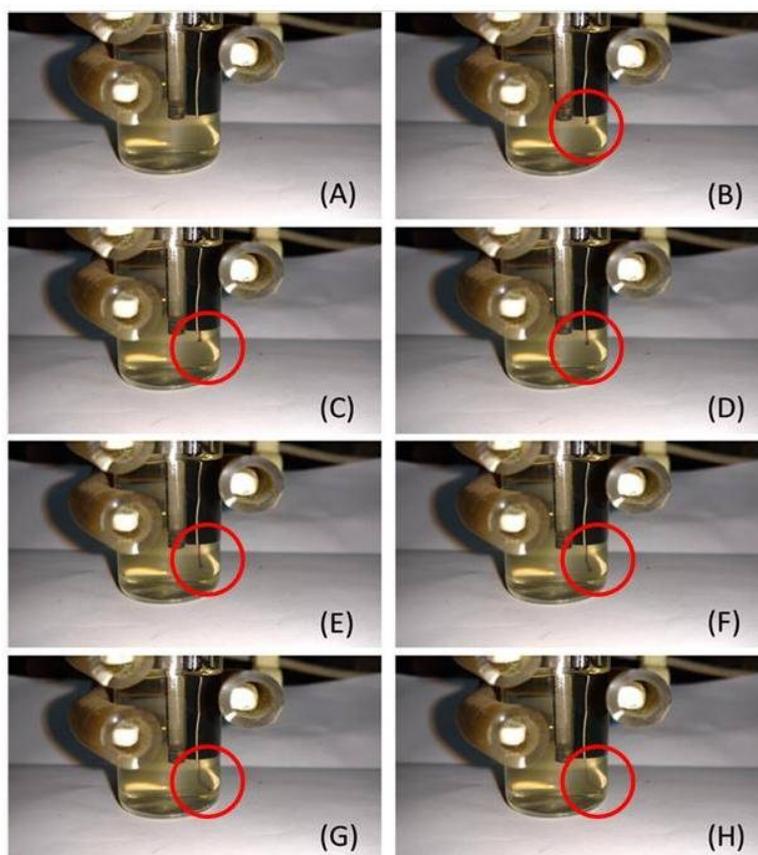
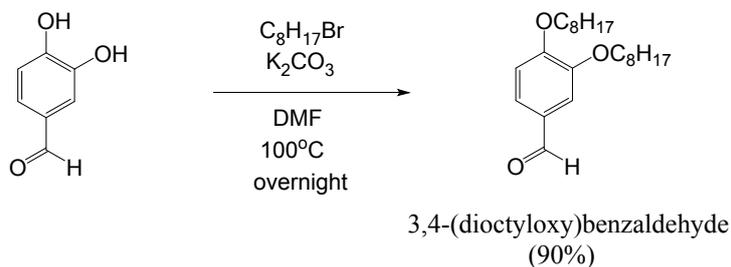


Figure S 4 Photographs of electro-chemical polymerization of compound **5** showing diffusion of the polymer being formed on the working electrode surface in to the electrolytic solution.

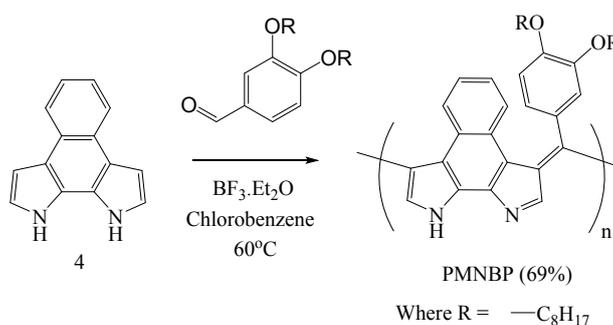
A similar behavior was observed in the case of the electro-chemical polymerization of compound **2**, and both of these behaviors can be explained by the stability of the cationic intermediates as described earlier for compound **2**. Also the observed increase in the current intensity of the oxidation peak at +1.41 V was small compared to the same observed in the case of the electro-chemical polymerization of compound **4**. So we concluded that the compound **5** is getting electro-chemically polymerized on the working electrode surface,

when oxidized by applying anodic voltage but it is not forming an even layer of the electro-active polymer.



Scheme S 3 Synthesis of 3,4-(dioctyloxy)benzaldehyde from 3,4-(dihydroxy)benzaldehyde

3,4-(dioctyloxy)benzaldehyde was synthesized using a modification of the method reported by Elliott et al⁸. A mixture of 3,4-(dihydroxy)benzaldehyde (1 gm, 7.24 mmol), *n*-octylbromide (3.490 gm, 18.07 mmol), K₂CO₃ (8 gm, 57.92 mmol) and few crystals of KI was dissolved in DMF (35 ml) and stirred overnight at 100°C. Product mixture was quenched in ice cold water, neutralised with 1 M HCl solution, filtered and dried in high vacuum. The crude product was purified by column chromatography over silica gel using 10% ethyl acetate-pet ether as eluent. Product was obtained as off white solid in 90% yield. ¹H NMR (400 MHz, CDCl₃): 9.84 (s, 1H), 7.44-7.40 (m, 2H), 6.97, 6.95 (d, 1H), 4.11-4.05 (m, 4H), 1.89-1.82 (m, 4H), 1.51-1.47 (m, 4H), 1.39-1.30 (m, 18H), 0.91 (s, 6H). Other characterization data are according to the literature⁸.



Scheme S 4 Synthesis of PMNBP from compound 4 and 3,4-(dioctyloxy)benzaldehyde

PMNBP was synthesized according to the following procedure. Monomer naphthobipyrrole **4** (0.051 gm; 0.25 mmol) was dissolved in chlorobenzene (~ 20 mM solution) in a clean and dry two necked round bottom flask and stirred at 0°C for 5 min. The ~ 20 mM solution of 3,4-dioctyloxybenzaldehyde (0.104 gm; 0.28 mmol) in chlorobenzene was taken in the addition funnel, to which BF₃·Et₂O (45% solution in Et₂O, 0.54 mL, 2.00 mmol) was added. This solution was added drop-wise to monomer naphthobipyrrole solution at 0°C and then the



Figure S 10 ¹H NMR spectrum of Di-Boc protected compound 1

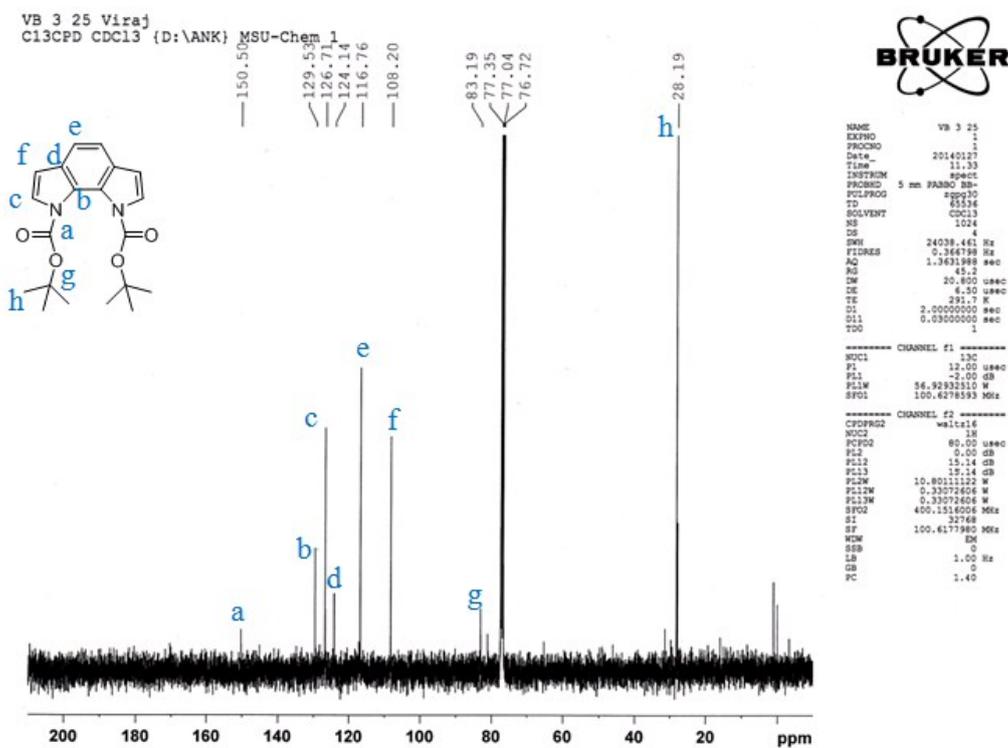


Figure S 11 ¹³C NMR spectrum of Di-Boc protected compound 1

DI-BOC-PROL #126 RT: 1.55 AV: 1 NL: 6.10E8
 T: + c Full ms [50.00-400.00]

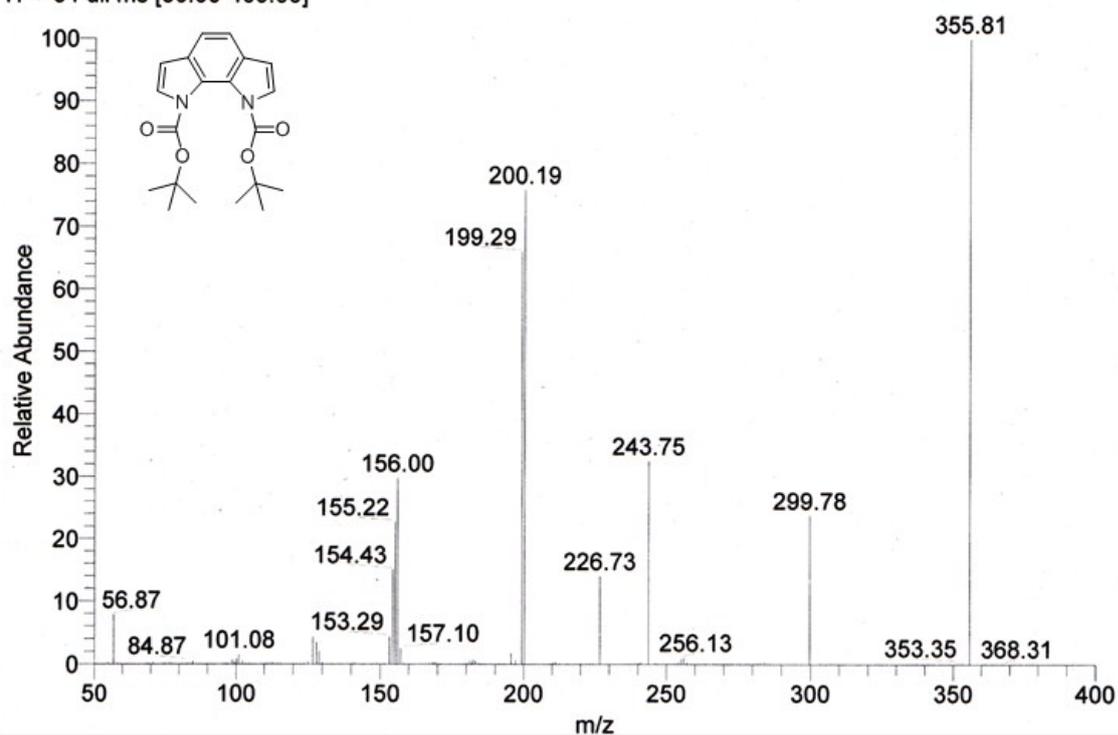


Figure S 12 ESI-Mass spectrum of Di-Boc protected compound 1; m/z calculated 356.17; found 355.81

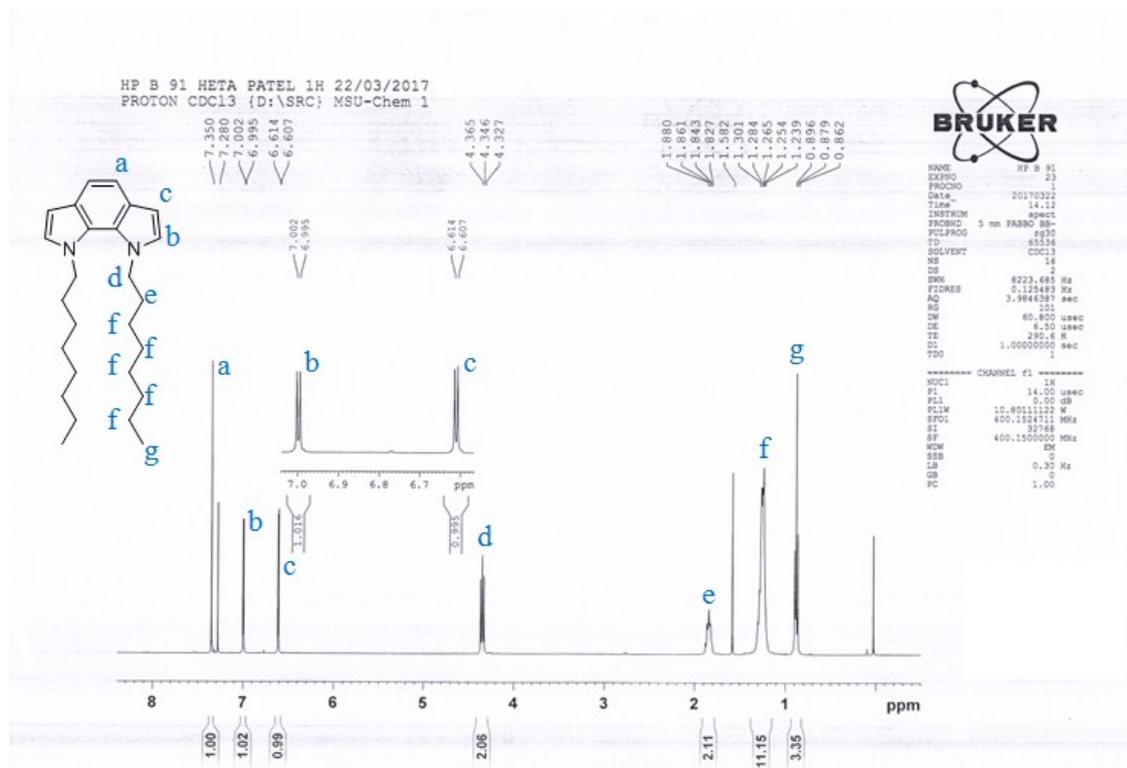


Figure S 13 ¹H NMR spectrum of compound 2

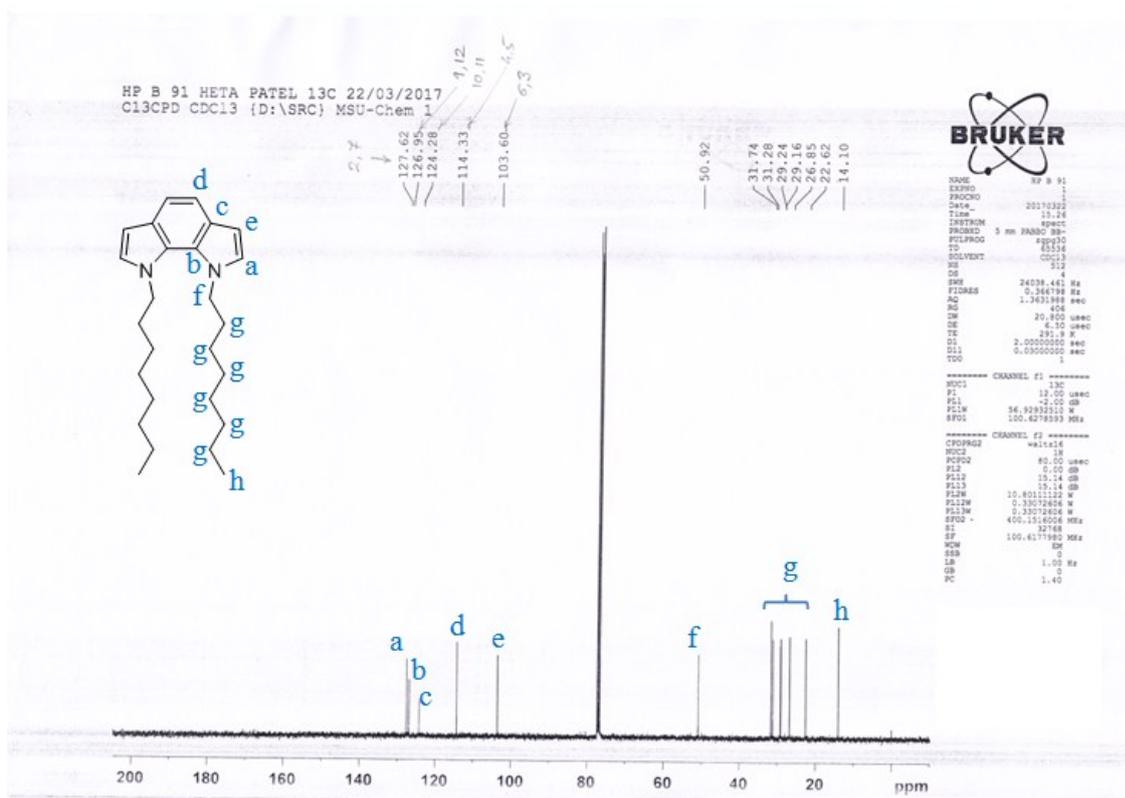


Figure S 14 ^{13}C NMR spectrum of compound 2

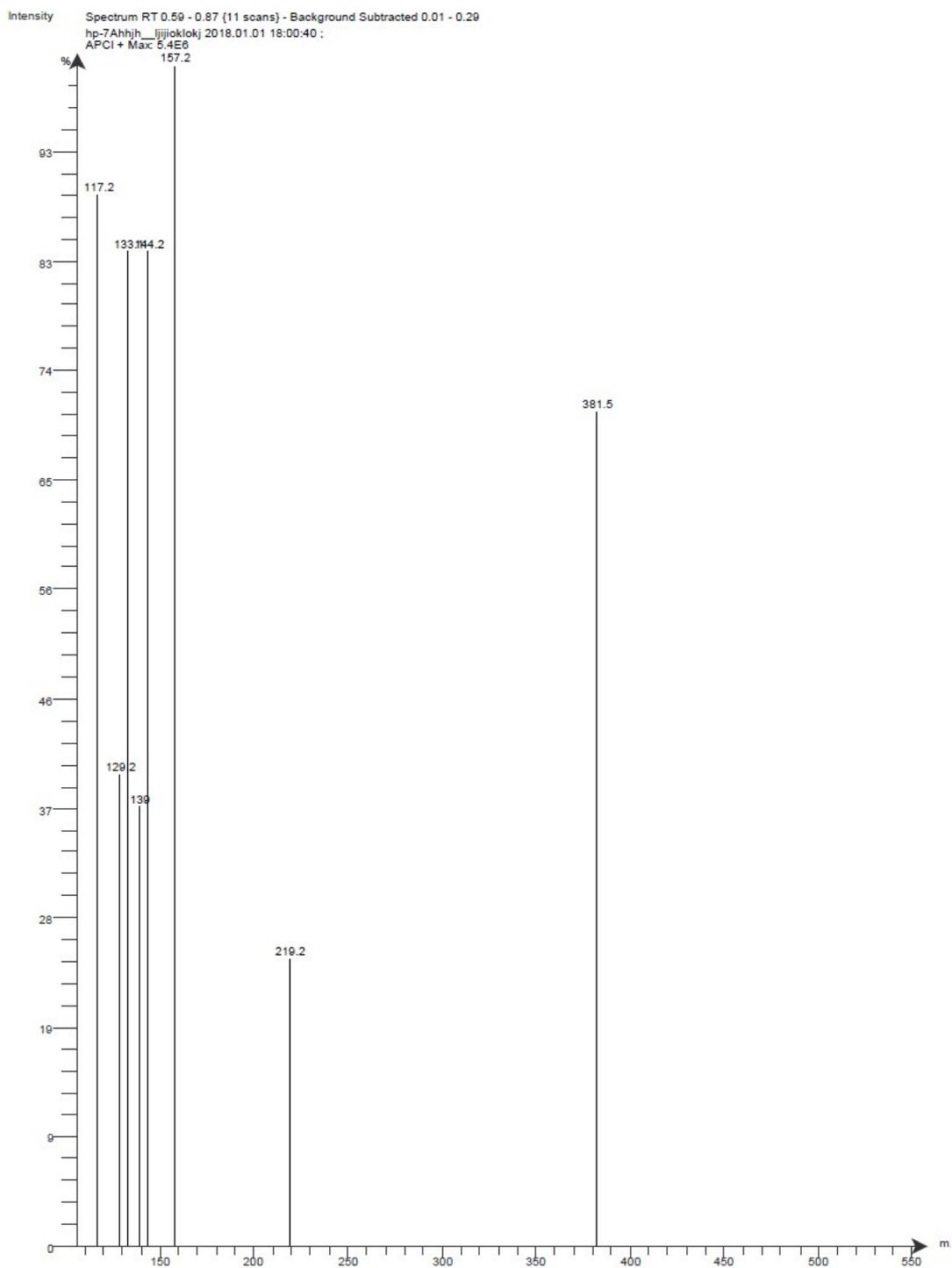


Figure S 15 ESI-Mass spectrum of compound 2; m/z calculated 380.6; found 381.5

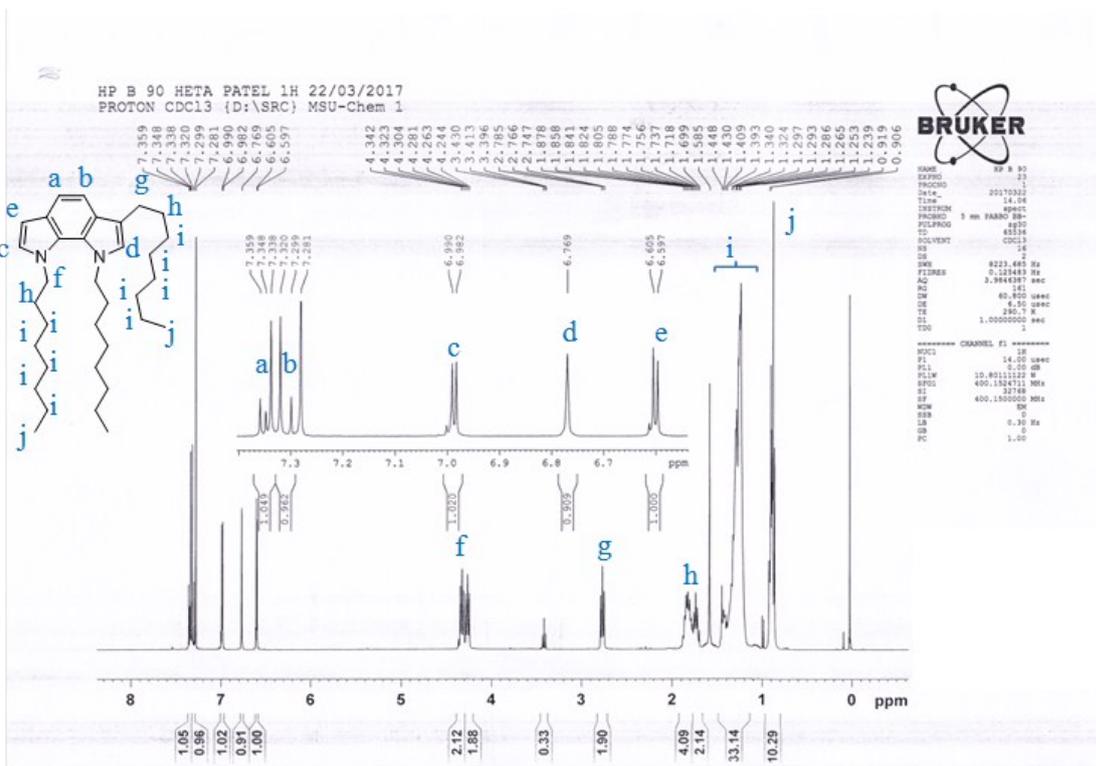


Figure S 16 1H NMR spectrum of compound 3

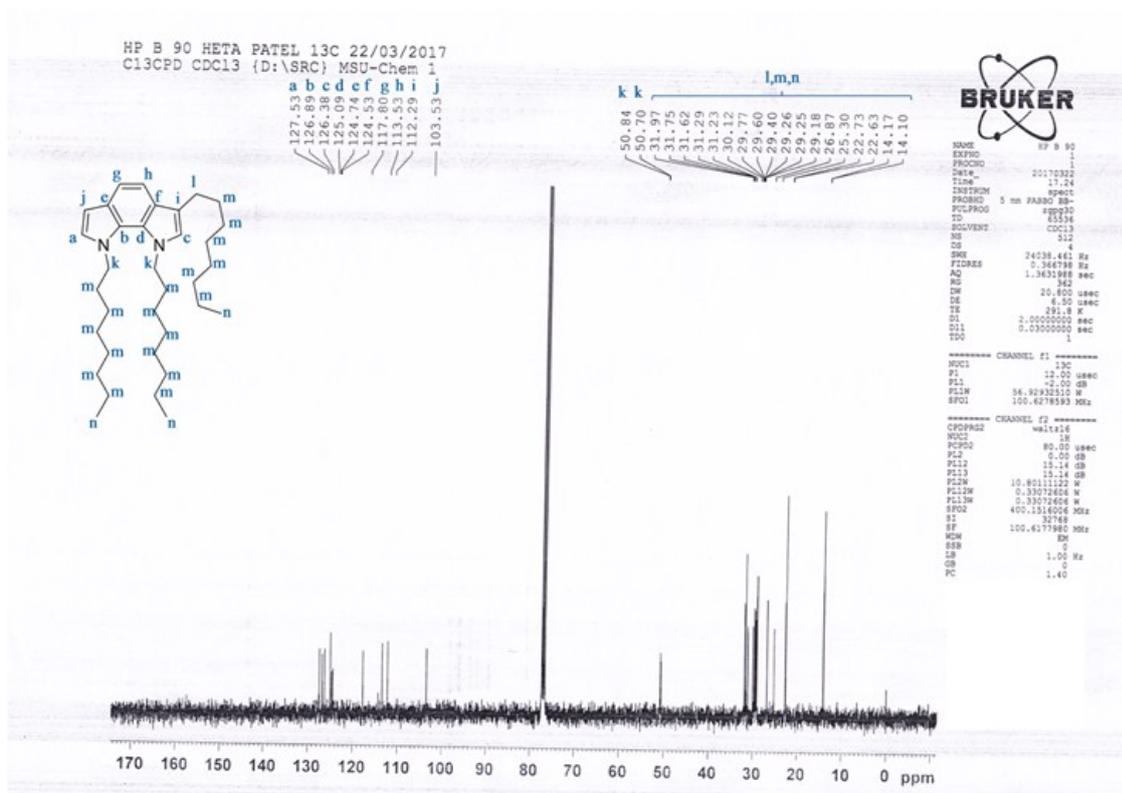


Figure S 17 13C NMR spectrum of compound 3

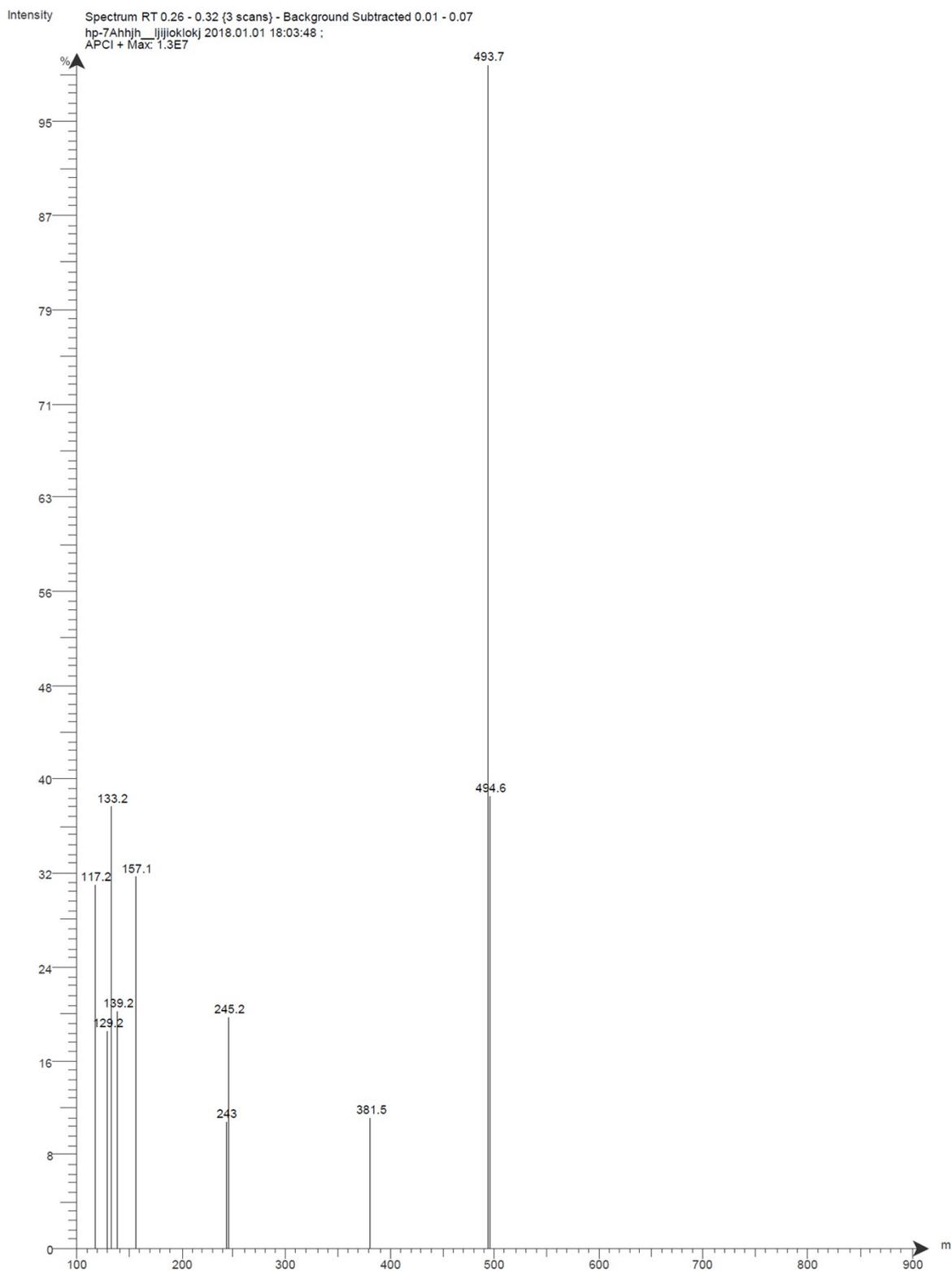


Figure S 18 ESI-Mass spectrum of compound 3; m/z calculated 492.6; found 493.7

BISHYDRAZONE #141 RT: 1.96 AV: 1 NL: 3.68E7
 T: + c Full ms [50.00-450.00]

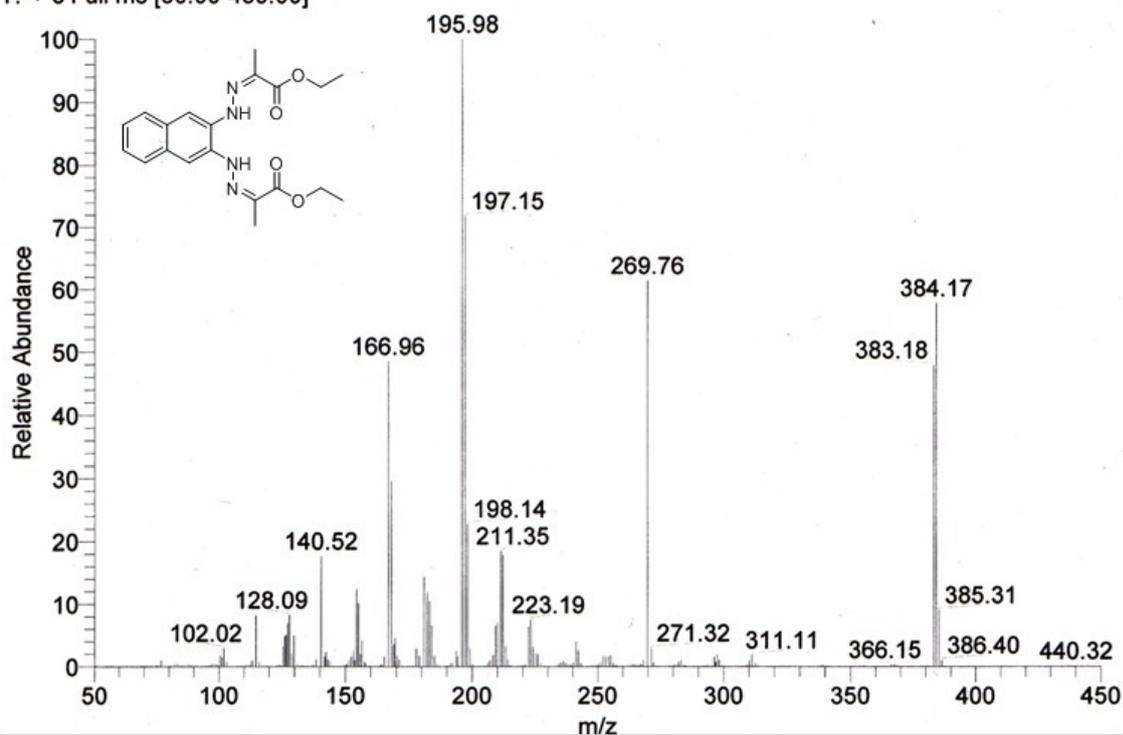


Figure S 19 ESI-Mass spectrum of compound 12; m/z calculated 384.18; found 384.17

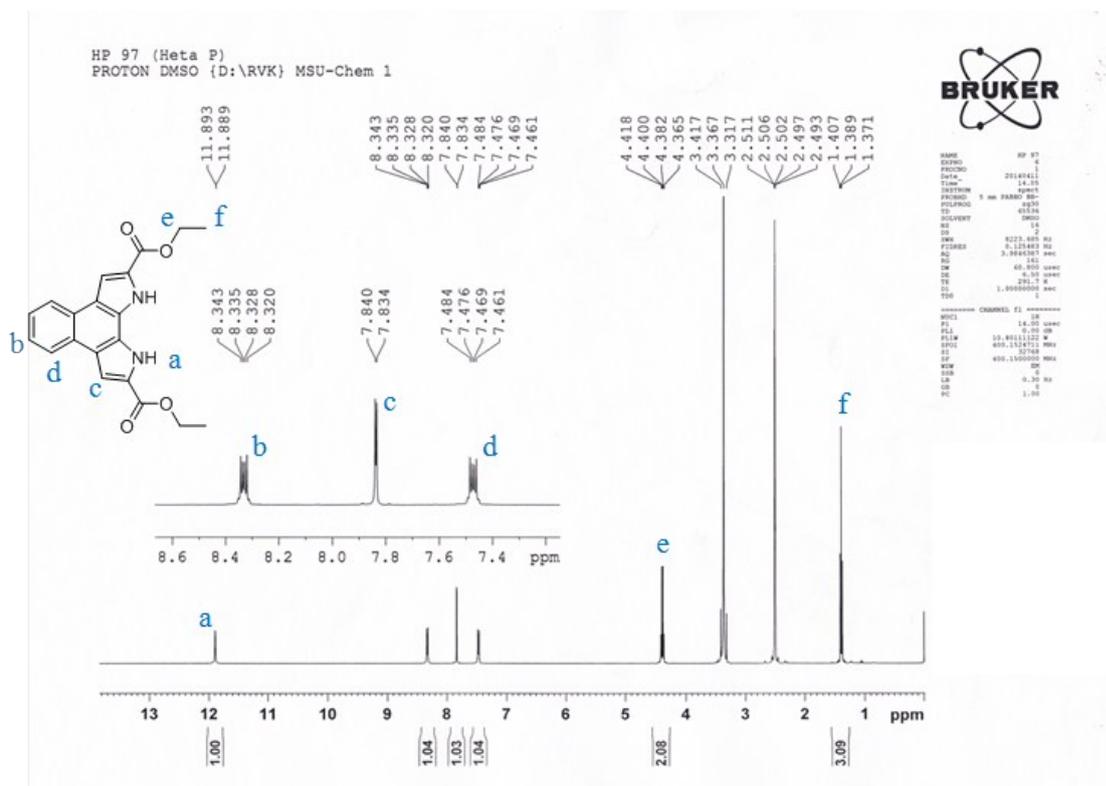


Figure S 20 ¹H NMR spectrum of compound 13

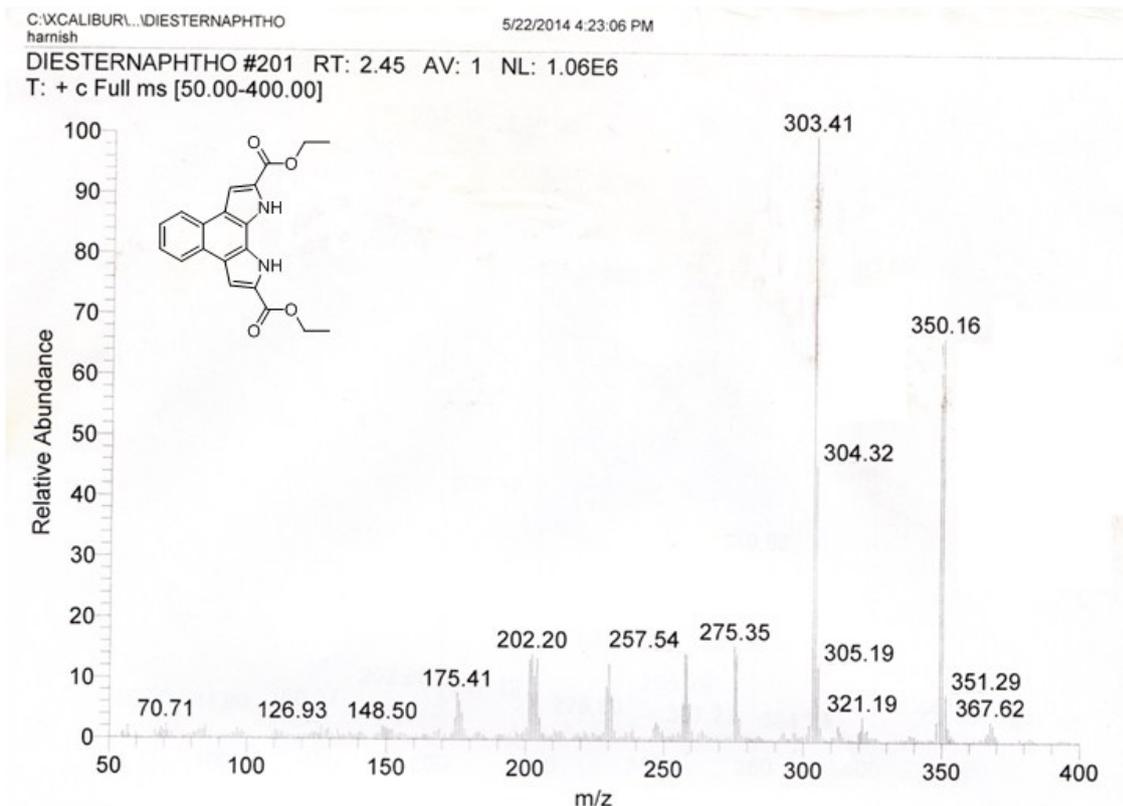


Figure S 21 ESI-Mass spectrum of compound 12; m/z calculated 350.13; found 350.16

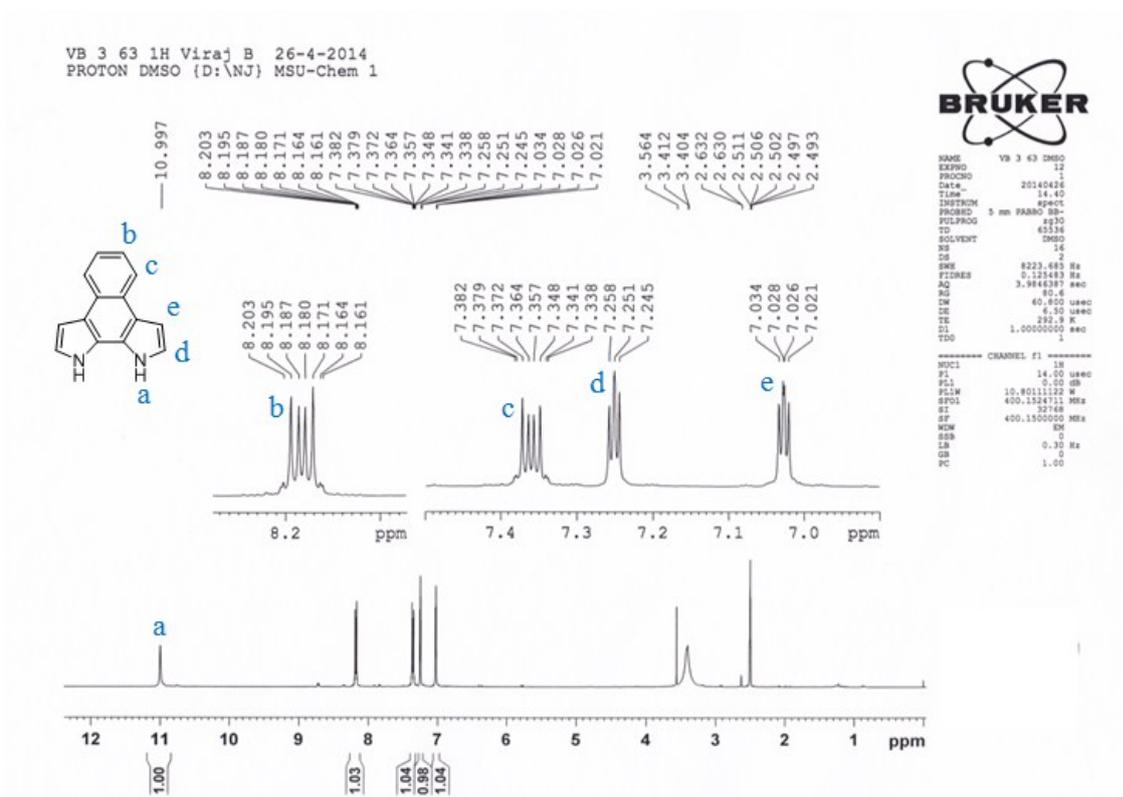
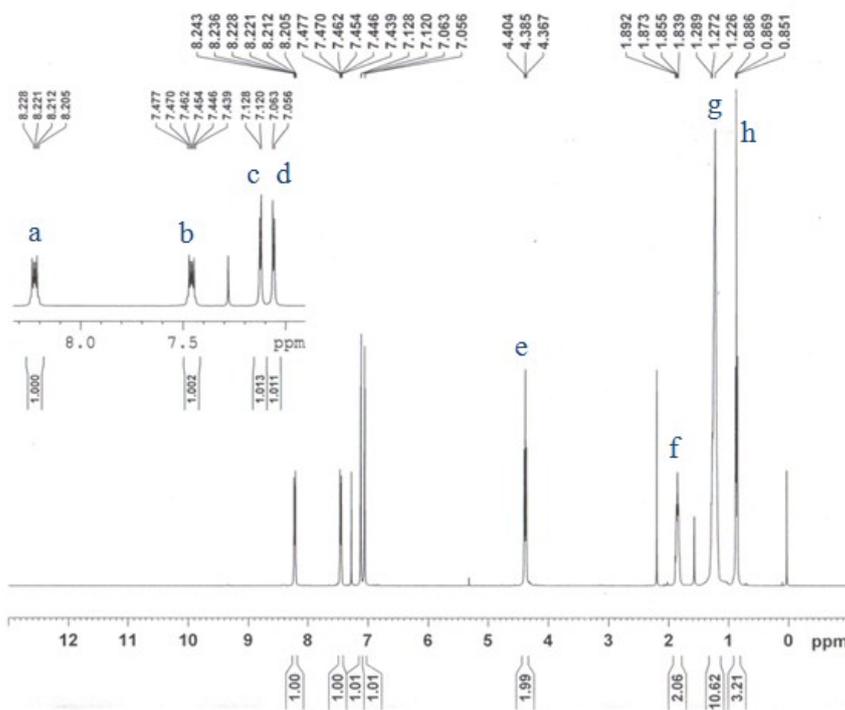


Figure S 22 1H NMR spectrum of compound 4

YH-2 YASH 1H 11-02-2017
 PROTON CDCl3 {D:\SRC} MSU-Chem 1



```

NAME      YH 2
EXPNO    6
PROCNO   1
Date_    20170211
Time     13.31
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        16
DS        2
SWH       8223.685 Hz
FIDRES   0.125483 Hz
AQ        3.9846387 sec
RG        71.8
DM        60.800 usec
DE        6.50 usec
TE        291.5 K
D1        1.00000000 sec
TDO       1
  
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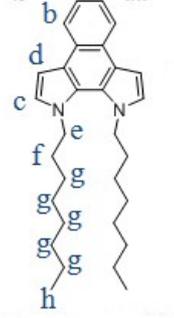
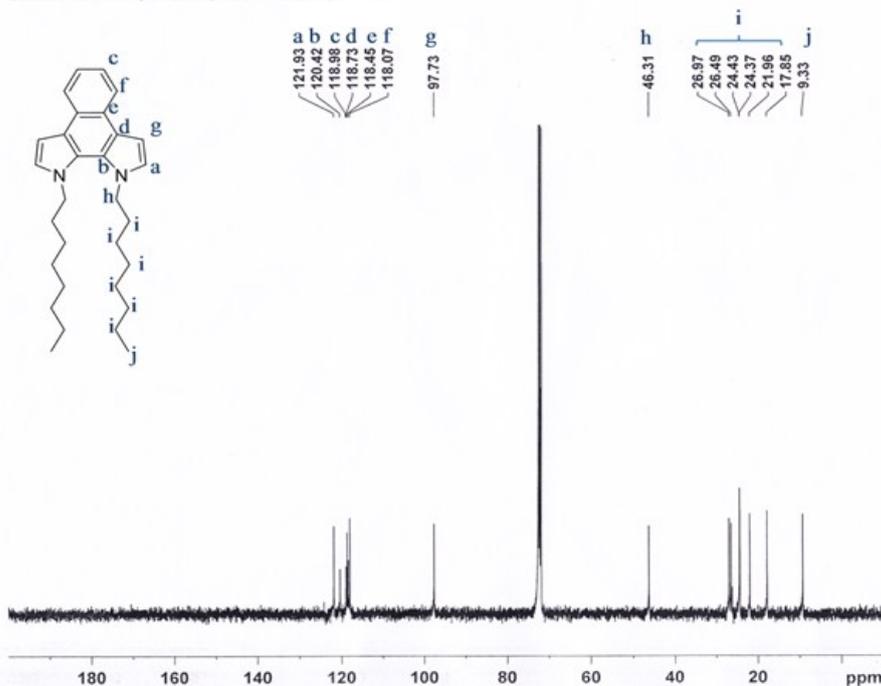


Figure S 25 1H NMR spectrum of compound 5

YH-2 YASH 13C 15-02-2017
 C13CPD DMSO {D:\SRC} MSU-Chem 1



```

NAME      YH 2
EXPNO    18
PROCNO   1
Date_    20170215
Time     13.11
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zgpg30
TD        65536
SOLVENT  DMSO
NS        1024
DS        4
SWH       24038.461 Hz
FIDRES   0.366798 Hz
AQ        1.3401988 sec
RG        45.2
DM        20.800 usec
DE        6.50 usec
TE        292.6 K
D1        2.00000000 sec
D11       0.03000000 sec
TDO       1
  
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Figure S 26 13C NMR spectrum of compound 5

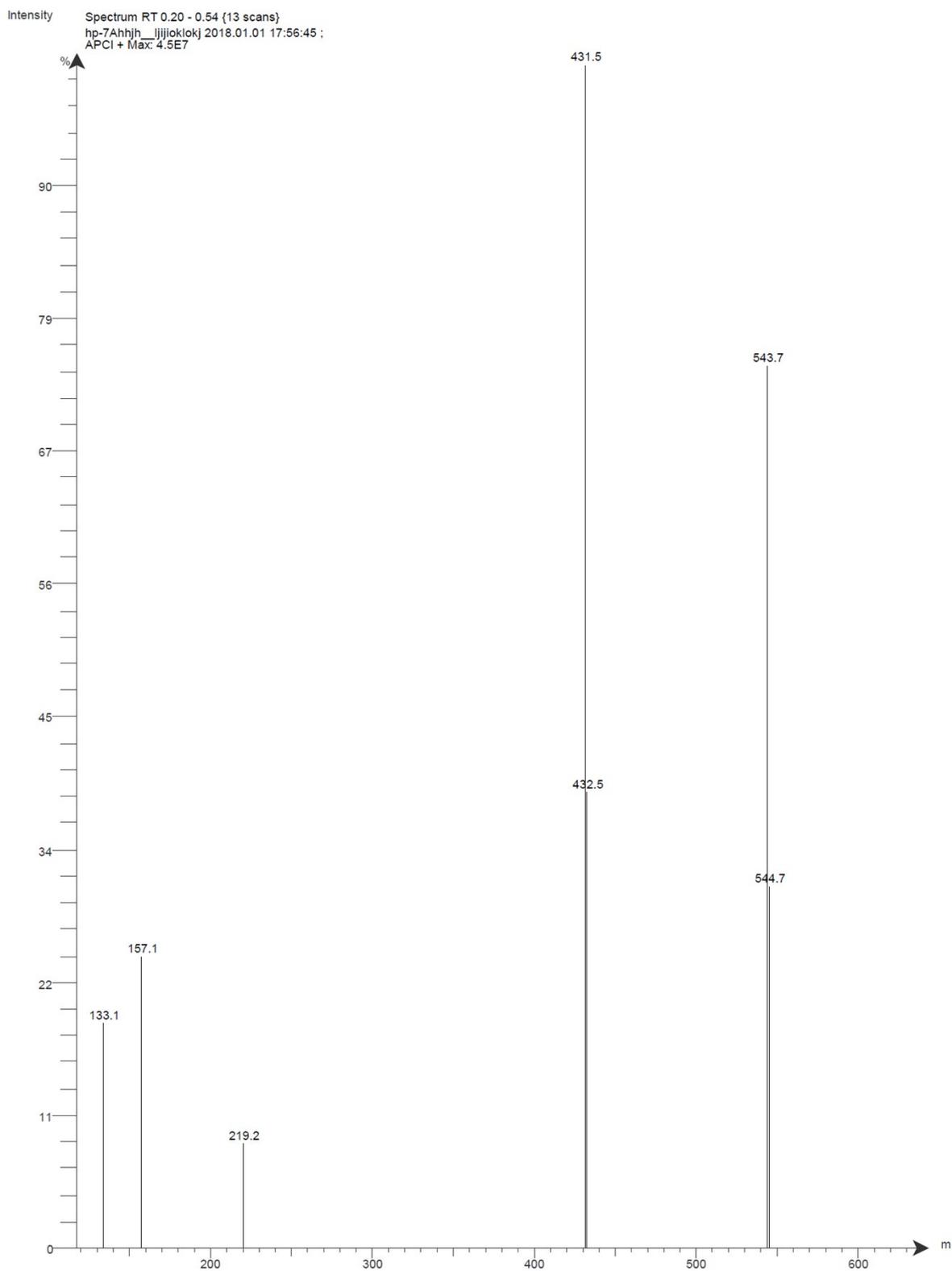


Figure S 27 ESI-Mass spectrum of compound 5; m/z calculated 430.6; found 431.5

Y-30 YASH 1H 04-02-17
 PROTON CDCl3 {D:\SRC} MSU-Chem 1

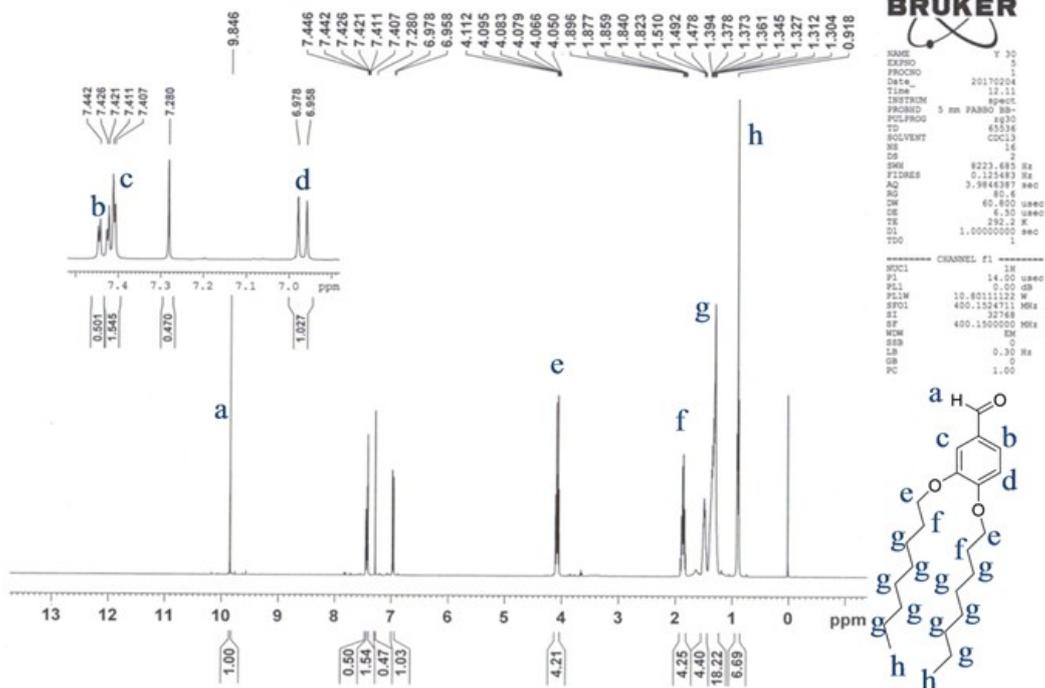


Figure S 28 ¹H NMR spectrum of 3,4-(dioctyloxy)benzaldehyde

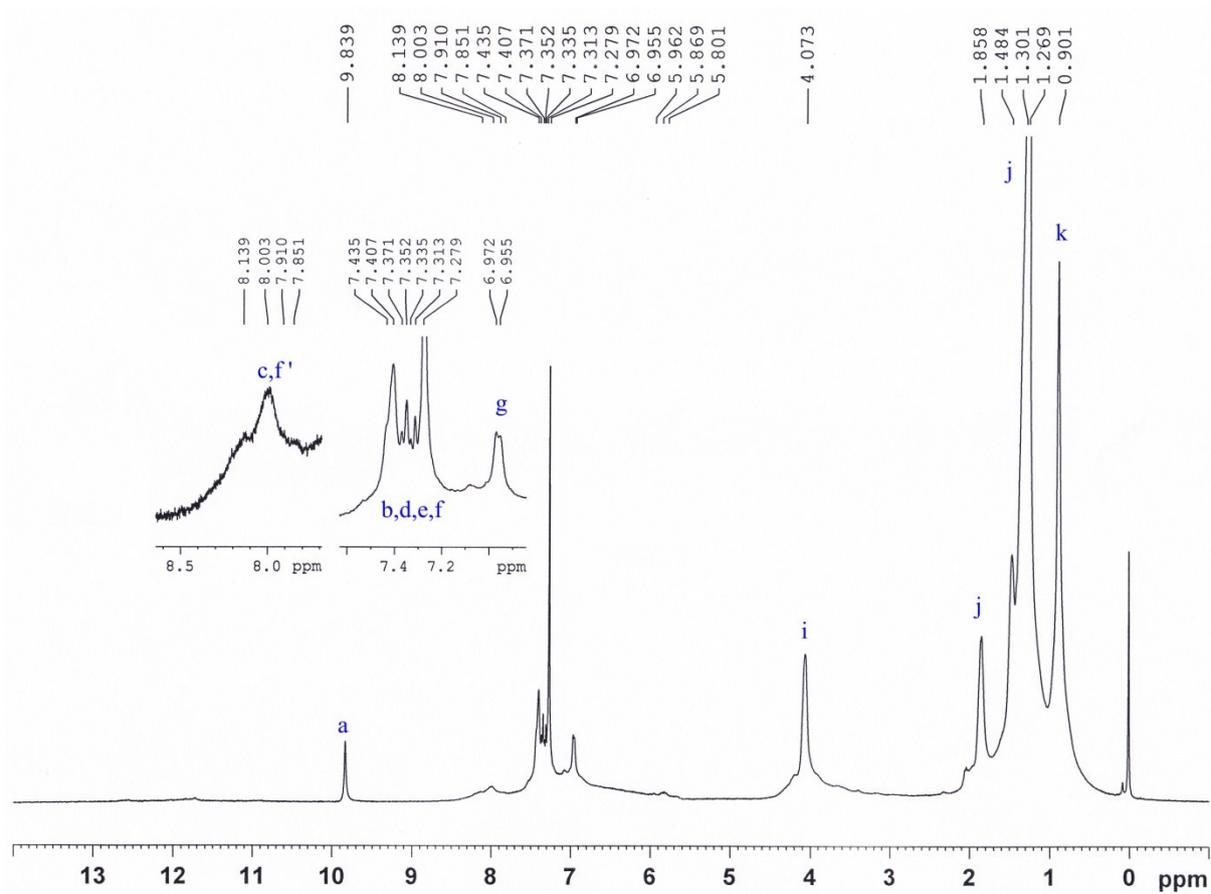
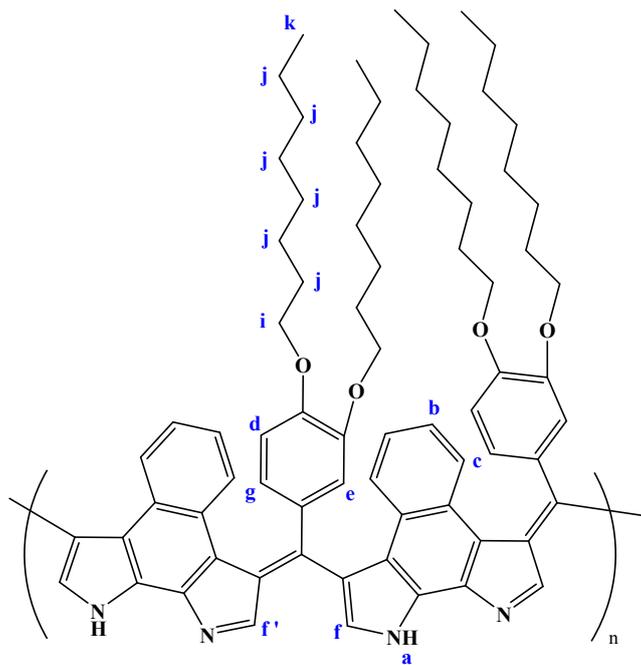


Figure S 29 ^1H NMR spectrum of PMNBP

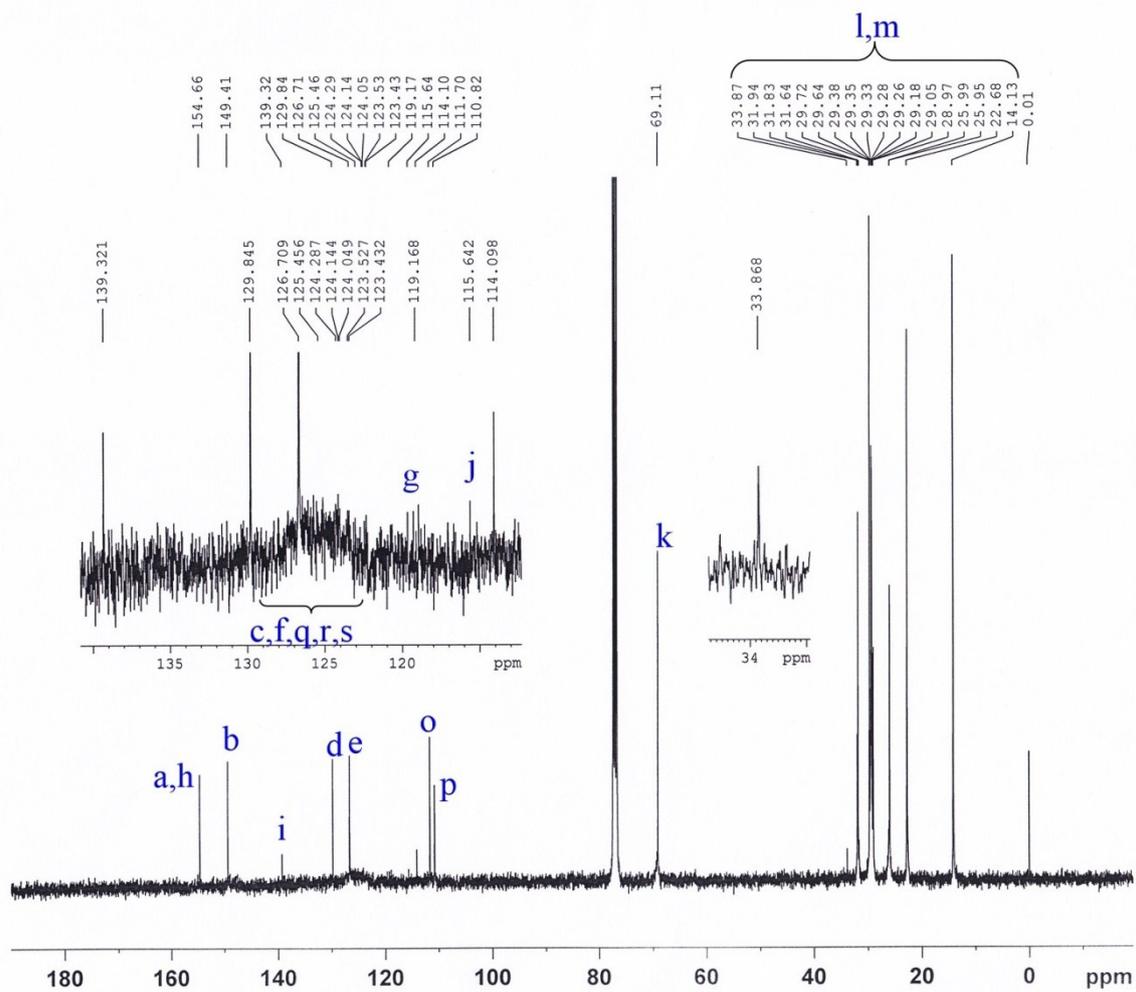
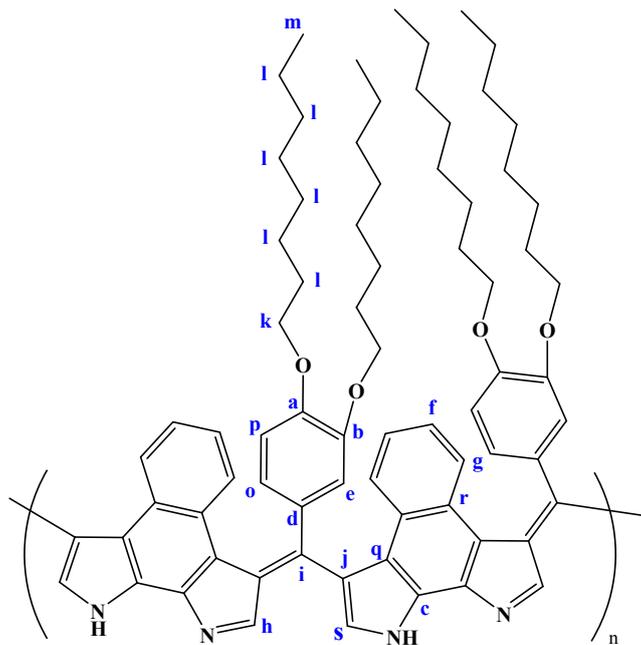
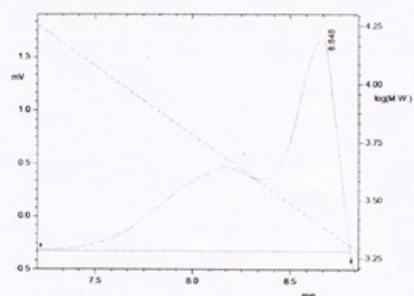


Figure S 30 ^{13}C NMR spectrum of PMNBP

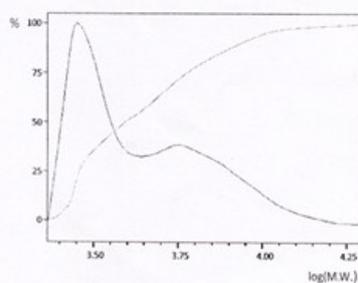
GPC Result Summary

Acquired by :PMNBP PL
 Sample Name :PMNBP PL
 Sample ID :PMNBP PL
 Vail# :64
 Injection Volume :10 µL
 Data Filename :3,4-PMNBP PL.04.lcd
 Method Filename :Polystyrene.lcm
 Batch Filename :
 Report Filename :Default.lcr

Chromatogram and Calibration Curve



Molecular Weight Distribution Curve



GPC Calculation Results

Peak#: 1 (Detector A Ch1)

[Peak Information]

	Time (min)	Volume (mL)	Molecular Weight	Height
Start	7.308	7.308	19054	-338
Top	8.646	8.646	2857	2126
End	8.808	8.808	2269	-334

Area : 58361
 Area % : 100.0000

[Average Molecular Weight]

Number Average Molecular Weight(Mn)	3996
Weight Average Molecular Weight(Mw)	4878
Z Average Molecular Weight(Mz)	6152
Z+1 Average Molecular Weight(Mz1)	7612
Mw/Mn	1.22072
Mv/Mn	0.00000
Mz/Mw	1.26117

D:\YMSUYArun\3,4-PMNBP PL04.lcd

Figure S 31 Gel Permeation Chromatography report of PMNBP

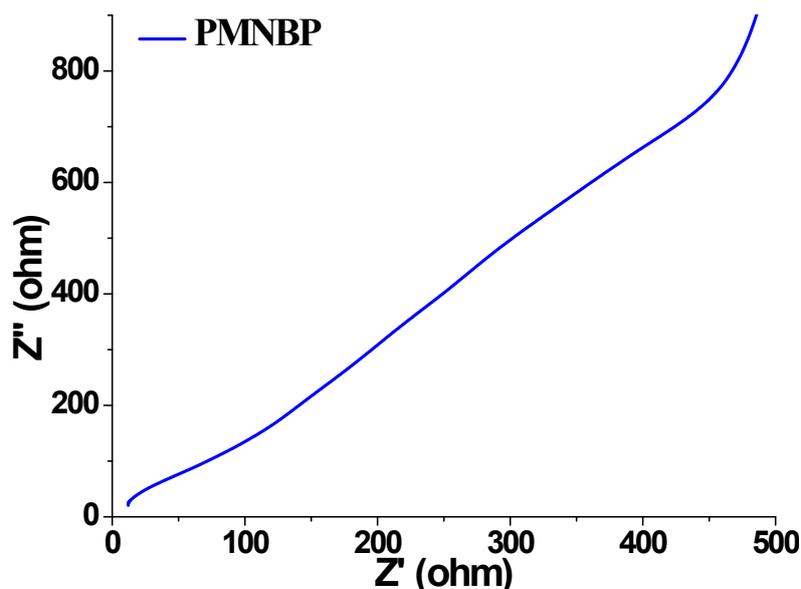


Figure S 32 Electrochemical Impedance Spectroscopy (EIS) plot of PMNBP, The conductivity was calculated from the equation, $\sigma = l/R_b A$, where σ , R_b , l , and A representing conductivity (mS cm^{-1}), ohmic resistance of the bulk material, distance between the two SS electrodes and the area of the electrodes respectively.

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